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APPLICATION NUMBER: 60/513,210
FILING DATE: *October 23, 2003*
RELATED PCT APPLICATION NUMBER: *PCT/US04/34496*

Certified by



Jon W Dudas

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Method and Apparatus for Converting Sulfur-Containing Distillates, and Compositions Obtained Thereby

This invention was made with Government support under Cooperative Agreement No. DE-FC26-01BC15281; W(A)-02-003, CH-1087 awarded by DOE. The Government has certain rights in this invention.

The US EPA and other environmental agencies (worldwide) have promulgated regulations that limit the sulfur content of fuels. The US EPA will soon limit sulfur content of "on-road" diesel fuel to 15 parts per million by weight (ppm_w). As a result of these regulations, there has been a significant research effort in the area of desulfurization.

Most large-scale refineries utilize hydrodesulfurization (HDS) to remove sulfur from fuels. HDS has traditionally been employed to produce fuels that contain less than 500-ppm_w sulfur. Many of the remaining sulfur compounds in such fuels are thiophenes, benzothiophenes, dibenzothiophenes, and their substituted analogs. Some of these compounds are difficult to desulfurize via HDS because they are sterically hindered. This is especially true for the 4, 6 alkyl-substituted dibenzothiophenes. These compounds are known to be the most refractive sulfur compounds in middle distillate fuels.

In general, the refractive sulfur compounds require an HDS unit to operate at higher temperatures (>650°F) and pressures (>1000 psig) and reduced space velocities.. Under these conditions, the reaction pathway consumes large amounts of hydrogen in order to saturate aromatic rings and double bonds, and open ring structures before the hydrogen can react with a sulfur atom. All of these factors tend to increase operating and capital costs.

Because of these shortcomings, interest in oxidative desulfurization has increased in recent years. Oxidative desulfurization operates at mild temperatures (< 212°F) and pressures (<30 psig). Several patents have been granted describing oxidative desulfurization techniques. These processes typically rely on a reaction step followed by a separation step.

The physical properties of organosulfur compounds found in hydrocarbon fuels are often very similar to the fuel itself. For example, middle distillate fuels such as atmospheric or vacuum gas oils are produced via

distillation. The organosulfur compounds that are contained in these gas oils have the same boiling range as the fuel itself. In fact sulfur compounds are found throughout the boiling range of the fuel. Therefore separation of the organosulfur compounds by distillation is not possible.

It is well known that a chemical reaction between thiophenic compounds and a suitable oxidizer can transform the original sulfur bearing compounds to their corresponding sulfoxides or sulfones. The addition of one or two oxygen atoms to the sulfur atom results in significant changes to several physical properties. For example, the physical properties such as polarity and volatility are changed. These changes in the physical properties enable the separation of the now oxidized sulfur bearing compounds from the hydrocarbon fuel. Separation techniques can rely on many physical properties, the two mentioned properties are not exhaustive but are mentioned for illustrative purposes.

Conventional processes related to oxidative desulfurization involve an oxidation reaction, where organosulfur compounds are converted to their respective sulfoxides and sulfones followed by one or more separation steps. Extraction and adsorption (either alone or in combination) typically make up the separation steps.

The inventors have found that many fuels contain a broad spectrum of organosulfur compounds. The original organosulfur compounds give rise to a broad spectrum of sulfoxides and sulfones. When processing fuels with approximately 5000-ppm_w sulfur content, for economic reasons, it may be desirable to optimize the duty of the extraction and adsorption processes. The inventors found that it is economically advantageous to remove most of the sulfur compounds utilizing extraction. Operating the extraction step for high sulfur removal leads to high solvent to feed ratios. Recovery of the solvent after extraction does not pose major difficulties. However the resultant extract is not only rich in sulfur compounds, but also contains sulfur-free fuel components, particularly aromatic compounds. The quantity of fuel lost via the extract ranged from 20 to 35 %. Further processing of the extract stream in other refinery units or to burn the stream for its energy value or use the stream as an asphalt modifier may be carried out.

The inventors found that downgrading the extract stream (as feed to another refinery processing unit) results in a high economic penalty. The instant invention overcomes these difficulties and provides a new process that is economically attractive. One advantage of this process is the minimization of fuel loss. Other oxidative processes cannot achieve the low sulfur fuel yields made possible by the present invention.

The present invention inheres additional advantages over pre-extraction type processes, for example. These advantages include:

- (1) Favors fuel recovery over minimizing oxidant consumption,
- (2) Minimizes the circulation of extraction solvent,
- (3) Eliminates the need for an extract wash step,

(4) Minimizes corrosive catalytic acids in downstream lines and equipment.

Another advantage of the present process is essentially complete conversion in the reaction section. This desirably allows fuel recovery via distillation.

A schematic block flow diagram showing one preferred embodiment of the invention is given in Figure 1, attached, and described in more detail below.

The invention process is particularly suitable to treat middle distillate fuels that contain a broad array of sulfur compounds. The sulfur compounds may be present in per cent level concentrations. The oxidant is a peroxy-carboxylic acid. The inventors found that the carboxylic acid used to form the peroxy-carboxylic acid is optimally used as the solvent. If a different solvent is chosen, then two separate "Solvent Recovery & Purification" steps and two separate "Hydrocarbon Recovery" steps would be needed.

1. Reactor System

The first step in the process is to combine the oxidant solution in Stream A, the high sulfur feed in Stream B and the carboxylic acid or an aqueous solution of the carboxylic acid in Stream D in the "Reactor System". In this step, the organosulfur compounds in the fuel are converted to sulfoxides or sulfones. If the reactor conditions favor the formation of two liquid phases, then the heavy phase leaves via Stream C. Stream C is directed to the "Solvent Recovery & Purification" step. The light phase leaves the "Reactor System" via Stream E. If the reactor conditions are chosen so that only one phase forms then the entire contents of the "Reactor System" leaves via Stream E.

2. Extraction

The next step in the process is the "Extraction". The extraction may be carried out in any suitable liquid/liquid-contacting device. The fuel containing oxidized sulfur compounds in Stream E is contacted with the solvent in Stream D. The more polar sulfoxides & sulfones leave the "Extraction" step together with the solvent in Stream F. The raffinate leaves the "Extraction" step via Stream H. Stream H contains fuel with less sulfur compounds and some solvent.

3. Water Wash

The next step in the process is a "Water Wash". The purpose of this step is to remove residual solvent from the fuel. This step is accomplished by contacting the fuel with water in any suitable liquid/liquid-contacting device. Fuel enters this step via Stream H and Stream O. Water enters via Stream G. The heavy phase leaves via

Stream I. Stream I contains water and solvent. Stream I is directed to the "Solvent Recovery & Purification" step. The fuel, essentially free of solvent, leaves via Stream J.

4. Adsorption

The next step in the process is "Adsorption". This step may or may not be needed depending on the sulfur concentration remaining after extraction. The purpose of the "Adsorption" step is to remove the last traces of sulfur from the fuel. The fuel enters via Stream J and exits this step via Stream K. A number of solids have been found to be suitable for this step of the process including but not limited to refiner's clay. The regeneration of the adsorbent may be carried out in several ways. These methods involve the use of a carrier fluid and changes in temperature, pressure or concentration. These changes alter the equilibrium, and favors desorption of the adsorbed substance. If the extraction solvent is used for the regeneration, then the resultant stream may be directed to the "Solvent Recovery & Purification" step.

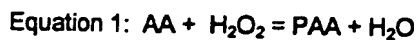
Bed regeneration may be utilized using the extract solvent and subsequent recycling to the front end of the process.

5. Solvent Recovery & Purification

The next step in the process is "Solvent Recovery & Purification". The purpose of this step is to recover and re-use the carboxylic acid that is used as the solvent and the precursor for the peroxy-carboxylic acid. The additional capital and operating expense of this step is less than the cost of purchasing fresh solvent. The "Solvent Recovery & Purification" step includes various unit operations, such as distillation and flash evaporation, designed to separate solvent from water or solvent from extract.

Solvent enters this step primarily via Stream F, Stream C, if present, and possibly via a regeneration step associated with the "Adsorption" step. Recovered solvent leaves via Stream D and is directed to the unit operations requiring solvent. Fresh solvent may be added to this stream or at other convenient points in the process to make up for losses.

Water with some solvent enters the "Solvent Recovery & Purification" step via Stream I. Water enters the process in Stream A and Stream G. Some water is also formed during the transformation of the carboxylic acid to the peroxy-carboxylic acid using hydrogen peroxide. For example acetic acid (AA) is transformed to peracetic acid (PAA) according to equation 1.



Hydrogen peroxide is commercially available as aqueous solutions. For these reasons water must be purged from the system via Stream M to prevent an accumulation of water. Some water may be recycled via Stream L. Depending on the operation of the "Solvent Recovery & Purification" step, a make up water stream may be needed. Make up water may be added to Stream L or at other convenient points in the process.

A small hydrocarbon phase may be generated during solvent recovery and purification. This stream may be processed through the "Water Wash" to improve yield.

6. Hydrocarbon Recovery

The next step of the process is "Hydrocarbon Recovery". Material is fed to this step via Stream N. Stream N is the extract (Stream F) with the solvent removed. Stream N contains the oxidized organosulfur compounds (sulfoxides and sulfones) and fuel components, and residual acetic acid. The fuel components are primarily the more polar aromatic compounds that boil in the diesel range. The "Hydrocarbon Recovery" step utilizes the volatility difference between the sulfoxides and sulfones and the aromatic fuel compounds. The inventors found that the boiling points of the oxidized sulfur compounds are beyond most of the compounds normally found in diesel. Distillation, vacuum distillation in particular, is a suitable unit operation for separating the fuel components from the oxidized sulfur compounds. The recovered fuel components are returned to the process via Stream O. The final extract leaves the process via Stream P.

One advantage of the present invention is realized by taking advantage of many of the physical property differences that are imparted to the organosulfur compounds once they are converted to their respective sulfoxides or sulfones. The instant invention is economically favorable and maximizes the fuel yield across the process.

One objective of the present invention is to convert straight run middle distillates containing various organosulfur compounds to a blending stock with less than 10 ppm_w of sulfur for addition to a refinery diesel pool. Preferably, for present purposes, the middle distillate considered is Light Atmospheric Gas Oil (LAGO). The blending stock may then be used in final fuel products such as diesel, jet, kerosene or light heating oils.

The process scheme utilized to meet this objective is based on the oxidation of sulfur containing organic species, followed by removal of the resulting polar organosulfur compounds using liquid-liquid extraction and solid phase adsorption.

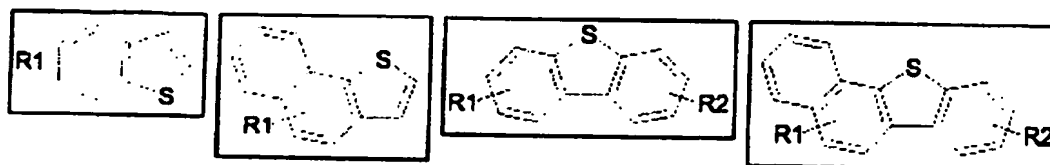
The economic feasibility of this scheme can best be realized if the fuel loss resulting from the extraction step can be minimized. The invention meets this economic requirement in-part by recovering extracted hydrocarbons via distillation.

By the present invention, significant hydrocarbon recovery via distillation can be achieved, particularly if the oxidation step is capable of essentially complete conversion of the organosulfur compounds to their oxidized forms. In their unoxidized form, the organosulfur compounds have the same boiling range as the rest of the hydrocarbons found in the distillate stream. If left unoxidized, these organosulfur compounds distill simultaneously with the hydrocarbons rendering distillation ineffective as a method to minimize yield loss. Once oxidized, the boiling points of these compounds are shifted significantly higher. This increase in the boiling points allows distillation to become a feasible method of hydrocarbon recovery.

The invention desirably alters the physical properties of the thiophenic compounds in LAGO via oxidation. These physical property changes result in higher polarities and higher boiling points. The process then takes advantage of these changes in the physical properties to separate the oxidized organosulfur compounds from the balance of the hydrocarbon fuel.

The process is particularly suitable for gas oil sulfur contents on the order of about 5100 ppm_w. However, it is possible to apply the same process to other middle distillate feeds with a lower or higher sulfur content, for example, from 5 to 500,000ppm, which includes 5, 10, 50, 100, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10,000, 20,000, 50,000, 75,000, 100,000, 200,000, 500,000, and any combination thereof. The process is particularly suitable for use in hydrotreated middle distillates. The process is also suitable for treating other middle distillates, however.

There are many organosulfur compounds in straight run LAGO. Typically, these organosulfur compounds have a fairly high molecular weight and belong to a general class of compounds called thiophenics. In most cases, these compounds are thiophene, benzothiophene, naphthothiophene, dibenzothiophene, naphthobenzothiophene, and their substituted homologues. Their respective molecular structures are shown below.



These organosulfur compounds are oxidized to sulfoxides and subsequently sulfones via reactions with active oxygen in the form of peracetic acid. In the invention process, the reactions are typically conducted at moderate temperatures (50 to 300F, which includes 50, 75, 100, 115, 120, 122, 125, 135, 145, 155, 165, 175, 185, 195, 200, 205, 210, 212, 214, 220, 250, 275 and 300F, and any combination thereof) and essentially atmospheric pressure. In this temperature range, the reaction mixture preferably includes two liquid phases.

The oxidation reactions could be conducted in a single-phase mixture by utilizing a higher temperature or by changing the acetic acid concentration in the fuel.

In the present application, the R, R1 and R2 groups may each independently be hydrogen or any substituent so long as the boiling point of the substituted compound is in the same range as the stream that is being processed. Preferably, the R, R1, R2 groups may each independently be linear or branched, cyclic or aliphatic, substituted or unsubstituted C1-C20 alkyl group, substituted or unsubstituted C7-C30 aryl group, C7-C30 arylalkyl group, and combinations thereof. This includes those having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, and 30 carbons, and any combination thereof as appropriate.

Preferably, the heavy phase is more polar than the light phase. Preferably, the heavy phase has a specific gravity of about 1. The heavy phase may suitably contain one or more of acetic acid, hydrogen peroxide, peracetic acid, water, sulfuric acid, soluble hydrocarbons, and soluble thiophenic compounds, in any combination. The dominant species in the heavy phase is acetic acid. Without wishing to be bound by theory, it is believed that the formation of peracetic acid most likely occurs in the heavy phase. Once formed, a portion of the peracetic acid migrates to the light phase.

Preferably, the light phase is less polar than the heavy phase. Preferably, the light phase has a specific gravity of less than about 1. The light phase preferably includes mostly hydrocarbons with a significant amount of acetic acid, and relatively small amount of one or more of peracetic acid, hydrogen peroxide, water and sulfuric acid in any combination.

Without wishing to be bound by theory, it is believed that the oxidation of thiophenic compounds to sulfones probably occurs in both the light and heavy phases. The formation of sulfones is very fast in the heavy phase, since the concentration of peracetic acid is relatively high. In the light phase, oxidation rates are slower, especially as the concentration of unoxidized sulfur-containing compounds approaches zero.

The reaction paths may be quite complex involving both reaction kinetics and mass transfer effects. Intimate contact between the two liquid phases in the reaction mixture is preferred for obtaining a sufficient rate of transfer of the peracetic acid between the two phases.

Peracetic Acid Formation:



Peracetic acid is formed via an equilibrium reaction between hydrogen peroxide and acetic acid. In addition to peracetic acid, water is formed as a byproduct. The reaction is slightly exothermic liberating approximately 348 calories per g-mole of peracetic acid formed.

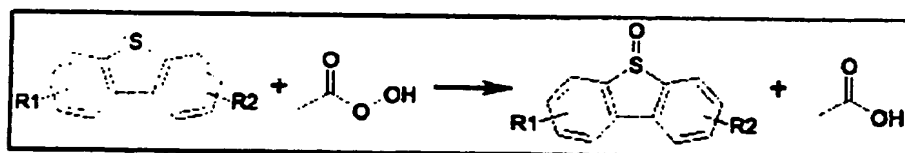
At room temperature, without the aid of a catalyst, the reaction is extremely slow and equilibrium concentration may take many hours to achieve. Higher temperatures can be utilized to accelerate the reaction rate within limits. Above 194 °F, decomposition of both the hydrogen peroxide and the resulting peracetic acid begins to become significant.

Significant increases in reaction rate without significant losses due to decomposition can best be achieved by using a catalyst. Typically, a strong acid catalyst is utilized. In the invention process, sulfuric acid is preferably used to catalyze the formation of peracetic acid. The reaction can be carried out without a catalyst. The use of other acids are possible including one or more mineral acids such as hydrochloric, nitric, phosphoric, organic acids such as formic, oxalic, or other proton donating substances including solids such as resins. These acids may be used alone or in any combination as appropriate.

At the reaction temperatures, hydrogen peroxide, acetic acid, and sulfuric acid concentrations used in the invention process, near reaction equilibrium conditions may be achieved within 2 to 5 minutes and approximately 90% of the hydrogen peroxide has been converted to peracetic acid. A large excess of acetic acid is preferred to favor the product side of the equilibrium reaction.

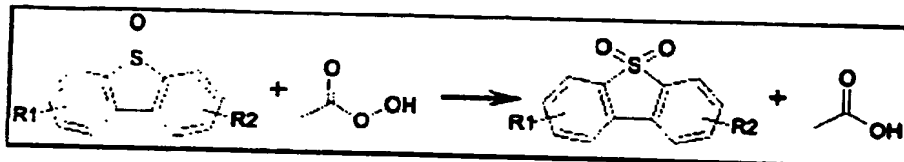
Sulfoxide Formation:

Oxidation of the thiophenic compounds occurs in two reaction steps. In the first step, thiophenic compounds react with peracetic acid to form a sulfoxide. Acetic acid is generated as a byproduct. This reaction is irreversible and highly exothermic. At relatively high thiophenic concentrations, this reaction is very fast. The reaction shown below depicts the oxidation of a generic dibenzothiophene. Similar reaction stoichiometry occurs for benzothiophenes, naphthothiophenes, and naphthobenzothiophenes.



Sulfone Formation:

In the presence of peracetic acid, the sulfoxide, once formed, is quickly oxidized to the sulfone. As in the formation of the sulfoxide, the formation of the sulfone also results in the production of acetic acid. This reaction is also irreversible, highly exothermic, and very fast. The reaction shown below depicts the oxidation of a generic dibenzothiophene sulfoxide. Similar reaction stoichiometry occurs for benzothiophene sulfoxides, naphthothiophene sulfoxides, and naphthobenzothiophene sulfoxides.



The literature on the oxidation of thiophenic compounds utilizing peracetic acid indicates that the formation of the sulfoxide is the rate-limiting step when considering the oxidation only. For dibenzothiophene, the relative difference in reaction rate of thiophenics with respect to sulfoxide is approximately 1.4. Namely, the oxidation rate of dibenzothiophene sulfoxide to dibenzothiophene sulfone is 40% greater than the oxidation rate of dibenzothiophene to dibenzothiophene sulfoxide. Therefore, once formed, the sulfoxide is quickly oxidized to the sulfone.

In the oxidation of the thiophenic compounds contained in LAGO, many reactions are occurring in parallel and series. Some thiophenic species are much more reactive than others. Laboratory studies on single model compounds indicate that the reactivity of the thiophenic compounds increases as the aromatic nature of the compounds increases and as the aromatic substitution increases. Namely, benzothiophene is less reactive than dibenzothiophene, which in turn is less reactive than naphthobenzothiophene and dibenzothiophene is less reactive than methyl dibenzothiophene, which in turn is less reactive than dimethyldibenzothiophene. The nature of these reactivity differences has been attributed to electronic density effects surrounding the aromatic sulfur atom. Increased aromatic character and aliphatic side chain substitution cause the electron density surrounding the sulfur atom to increase. This higher electronic density makes the sulfur atom more prone to attack by the peracetic acid molecule.

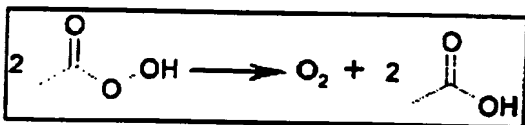
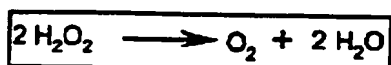
In a complex mixture like LAGO, this reactivity matrix results in a near continuous set of reaction rates. Under these circumstances, the possibility of minimizing the consumption of oxidant by selectively oxidizing to the sulfoxide is essentially futile. Kinetic studies on systems containing just five thiophenic species clearly indicate that the partial oxidation approach results in a marginal benefit.

Since the partial oxidation approach requires sub-stoichiometric quantities of oxidant (less than 2 moles of oxidant per mole of sulfur), near complete oxidation of the organosulfur compounds in LAGO is not possible under these circumstances. Without nearly complete oxidation, maximizing hydrocarbon yield via distillation

is not possible. In order to achieve total oxidation in a reasonable residence time, a sufficient amount of excess oxidant is required.

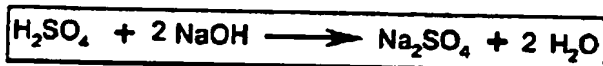
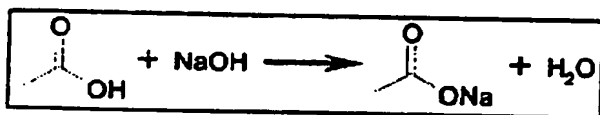
Destruct Reaction (optional):

After oxidation is complete, the heavy phase and light phase leaving the oxidation system still contain small amounts of excess active oxygen that should be removed. By elevating the temperature at specific points, both hydrogen peroxide and peracetic acid decompose. The reaction stoichiometry for each of these decompositions is shown below.



Neutralization Reaction (optional):

Two moles of water are formed for every mole of sulfur that is oxidized, and thus a wastewater stream is produced. This wastewater stream contains acetic acid and sulfuric acid that should preferably be neutralized before disposal. The neutralization is accomplished by utilizing sodium hydroxide. The products of this neutralization are sodium acetate and sodium sulfate. The use of other neutralizing salts and/or bases is possible.



The design is particularly suitable for a typical small to medium petroleum refinery that has limited or no hydrodesulfurization (HDS) capability.

One advantage of this process is that it is readily scaled. Plants can be designed with smaller or larger capacities. Capacities as small as 1 to 2 barrels per day to as high as 500,000 barrels per day are possible.

The feed desirably contains 5,100 ppm_w of sulfur in the form of thiophenic compounds including benzothiophene, dibenzothiophene, naphthobenzothiophene, and several of their substituted homologues. This corresponds to a thiophenic composition of 2.89 wt %. The aliphatic content of the feed is 66.4 wt % while the non-sulfur containing aromatic content of the feed is 30.7 wt %.

The gas oil may be suitably delivered at 50 psig and 68 °F.

Preferably, the oxidant used in the process is stabilized 70 wt% hydrogen peroxide in water.

Preferably, the solvent used in the process is glacial acetic acid (greater than 98 wt% acetic acid).

Preferably, the catalyst used in the process is 98 wt% sulfuric acid in water, which may be suitably delivered at 50 psig and 68 °F

Preferably, the neutralization agent is 25 wt% sodium hydroxide in water, which may be suitably delivered at 50 psig and 68 °F.

One preferred overview of the process follows the Block Flow Diagram (BFD) shown below.

Preferably, there are seven major unit operations in the invention process: Oxidation, Sulfox Extraction, Raffinate Washing, Raffinate Polishing, Solvent Flash / Solvent Recovery, Solvent Purification, and Hydrocarbon Recovery.

In the Oxidation System, the thiophenic compounds in gas oil are oxidized to sulfones. Preferably, the oxidation is accomplished with hydrogen peroxide in the presence of recycled acetic acid. The overall molar conversion of the organosulfur compounds is approximately 90 to 99.99%, and more preferably about 99.8 percent, and these ranges include 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.5, 99.8, and 99.9%. For every mole of sulfur present in the feed, a range of about 2.0 to 10.0 moles of oxidant, and more preferably about three (3) moles of oxidant, is preferred. This range includes all values and subranges therebetween, including 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5 and 10 moles. The preferred amount of oxidant is 50 percent more than the stoichiometric requirement necessary for complete conversion to the sulfone. The water formed by the reaction and the water that enters the oxidation system with the hydrogen peroxide are preferably separated from the oxidized gas oil and fed to Solvent Purification for recovery of acetic acid and purging of reaction water. The oxidized gas oil that is now saturated with acetic acid is fed to the Sulfox Extraction System.

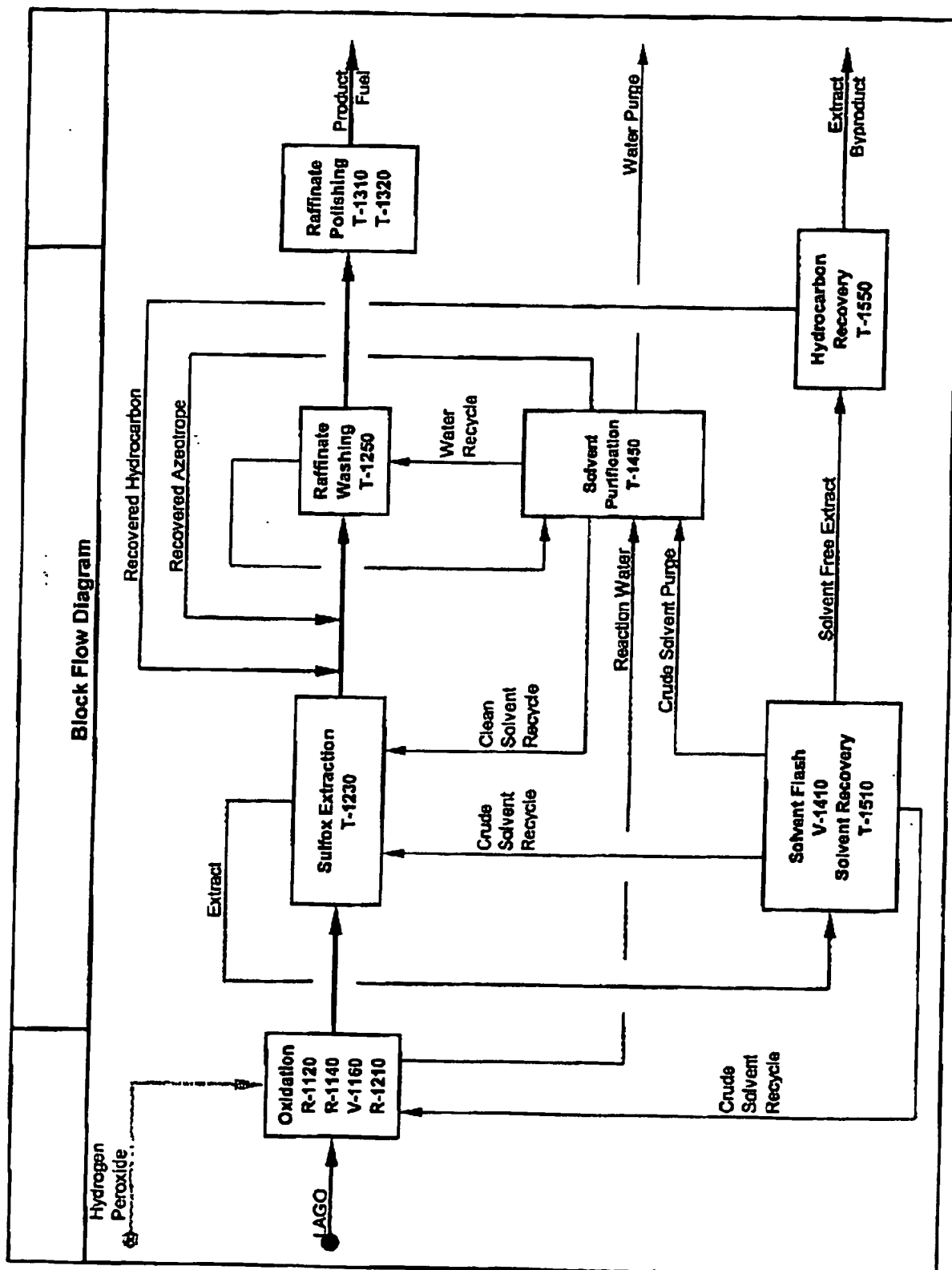
In the Sulfox Extraction System, the peracetic acid remaining in the oxidized gas oil is preferably first destroyed by heating. At temperatures above 200F, the peracetic acid in the gas oil decomposes rapidly to

oxygen and acetic acid and at temperatures above 230F decomposition is most preferred. The resulting gas oil is then fed to an extraction column where most of the oxidized organosulfur compounds are removed by contacting with recycle acetic acid. The preferred extraction temperature is 113 °F. The recycle solvent is mostly acetic acid and contains 0.6 wt% water and 5.4 wt% hydrocarbon. A sulfur removal of greater than 99 percent is obtained in this extraction step. The resulting extract that contains most of the oxidized organosulfur compounds is fed to the Solvent Flash / Solvent Recovery System. The gas oil raffinate that is still saturated with acetic acid and contains small amounts of organosulfur compounds is fed to the Raffinate Wash System.

In the Raffinate Wash System, acetic acid is suitably removed from the gas oil by contacting with water in a mechanically agitated extraction column. Preferably, the extraction is conducted at 113 °F and the resulting gas oil raffinate contains approximately 5800 ppm_w of acetic acid. The extract is fed to the Solvent Purification System for recovery of the extracted acetic acid and the purification of the water. The gas oil raffinate is fed to the Raffinate Polishing System.

In the Raffinate Polishing System, the remaining organosulfur compounds and acetic acid are removed from the raffinate gas oil in a solid bed adsorption column. Preferably, the adsorption beds are based on refinery clay. The ability of this material to adsorb sulfones has been demonstrated in the laboratory. Preferably, the resulting product gas oil contains less than 10 ppm_w sulfur and essentially no acetic acid.

In the Solvent Flash / Recovery System, acetic acid is removed from the extract produced in the Sulfox Extraction System. First, most of the acetic acid is removed and preferably in a single stage flash. The resulting extract, containing approximately 15 wt% acetic acid is then fed to a small distillation column. In this column, the acetic acid content of the extract is reduced to approximately 2 wt% before being fed to the Hydrocarbon Recovery System. The recovered acetic acid from the single stage flash and the distillation column are combined. This recovered acetic acid contains light hydrocarbons that form minimum boiling homogeneous azeotropes with the acetic acid. Most of the recovered acetic acid is recycled to the Oxidation System and to the Sulfox Extraction System. However, in order to control the build up of azeotropic hydrocarbons in these recycle loops, a portion of the recovered acetic acid is preferably fed forward to the Solvent Purification System.



In the Solvent Purification System, a distillation column is utilized to separate acetic acid from water and azeotropic hydrocarbons. The feed streams to this distillation column include the acetic acid / water stream generated in the Oxidation System, the acetic acid / water stream generated in the Raffinate Wash System, and the acetic acid / hydrocarbon stream generated in the Solvent Flash / Recovery System. Due to the high water content and reduced acetic acid content, the distillate resulting from this column is a heterogeneous azeotrope. Upon condensing, two liquid phases result. The hydrocarbon rich phase is combined with the gas oil feed to the Raffinate Wash System for recovery of the hydrocarbon and recovery of the acetic acid. The water phase that contains small quantities of acetic acid and small quantities of hydrocarbon is split into two streams. One stream is purged from the system. This stream preferably includes the water that enters the system with the hydrogen peroxide and the water generated from the formation of peracetic acid. The other water stream is recycled to the Raffinate Wash System as the extraction solvent.

In the Hydrocarbon Recovery System, the concentrated extract from the Solvent Flash / Recovery System is distilled under vacuum to recover the hydrocarbon content. Vacuum distillation is preferred due to the high boiling points of the sulfones contained in this extract stream. The overhead product from this distillation is hydrocarbon with 2.7 wt% acetic acid. This material is combined with the gas oil feed to the Raffinate Wash System for recovery of the hydrocarbon and the recovery of the acetic acid. The material leaving the bottom of the vacuum distillation is a combination of hydrocarbon and sulfones. The sulfone content is approximately 32 wt%. This vacuum distillation recovers approximately 80 percent of the hydrocarbon in the feed to this system. As a result, the overall hydrocarbon yield for the entire process is 90 percent. The overall hydrocarbon yield may be as high as 97 percent.

A more detailed description of the invention process follows in preferred embodiments and examples, which are not intended to be limiting.

Where appropriate, the discussions are accompanied by a detailed Process Flow Diagram (PFD). The normal material balances that accompany each PFD are also shown where appropriate. The normal heat balance for the process is shown on the individual PFDs in the form of stream & equipment temperatures, stream & equipment pressures and heat exchange duties. Where appropriate, the PFDs also include a preliminary control concept. This control concept indicates the primary control variables within the process.

Oxidation (PFD 003-20-211-1110)

In Oxidation, the organosulfur compounds in the gas oil feed are essentially completely oxidized to sulfones via reactions with active oxygen in the form of peracetic acid. The peracetic acid is formed in situ by reacting hydrogen peroxide with acetic acid. The overall conversion of thiophenic sulfur to sulfones is 99.8 %. Preferably, a total of 3.0 (2.0 to 10) moles of hydrogen peroxide per mole of sulfur are used in the oxidation.

The reaction mixtures in the Oxidation System includes two liquid phases. The formation of peracetic acid occurs in the heavy phase while the oxidation of organosulfur compounds to sulfones occurs in both phases. Sulfuric acid, hydrogen peroxide, and water primarily reside in the heavy phase. Acetic acid, peracetic acid, thiophenics, and sulfones distribute between both phases. Hydrocarbons primarily stay in the light phase, although some of the aromatic compounds and, to a lesser extent, some of the aliphatic compounds in the gas oil are soluble in the heavy phase.

The Oxidation System utilizes two reactors (R-1120 & R-1140), two decanters (V-1122 & V-1141), and a reboiled flash vessel (V-1160 & X-1161).

Fresh gas oil enters the unit via pipeline where it is first partially heated in X-1124 by a higher temperature downstream process fluid. Final reactor feed temperature is then obtained by heating the gas oil with 150-psig steam in X-1121. Recycle acetic acid from the Solvent Flash / Recovery System is added to the fresh gas oil. Approximately, one pound of recycle acetic acid is used for every five pounds of gas oil. The combined gas oil / acetic acid stream is then fed to the 1st Stage Oxidizer (R-1120). Recycle oxidant from the 2nd Stage Oxidizer (R-1140) is also fed to the 1st Stage Oxidizer. This recycle stream contains approximately 2.5 (1.8 to 3.0) moles of oxidant per mole of sulfur in the gas oil feed to the 1st Stage Oxidizer. In addition to oxidant, this recycle stream contains sulfuric acid catalyst. The temperature of the combined feed to the 1st Stage Oxidizer is about 176 °F (140 to 194).

Addition of acetic acid to the gas oil prior to contacting with oxidant is preferable for maintaining a relatively high concentration of peracetic acid in the heavy phase within the 1st Stage Oxidizer. Due to the relatively high acetic acid distribution coefficient, if the gas oil did not contain sufficient acetic acid, redistribution would occur when the oxidant solution contacts the gas oil. This redistribution would cause a decrease in the acetic acid concentration in the heavy phase. This in turn would cause some of the peracetic acid in the heavy phase to revert back to acetic acid and hydrogen peroxide in order to satisfy the reaction equilibrium conditions.

The presence of sulfuric acid in the 1st Stage Oxidizer is also preferred. When the oxidant solution contacts the gas oil, peracetic acid will distribute between the two phases. In the heavy phase, compensation for

departure from reaction equilibrium conditions can best occur if the rate of peracetic acid formation is relatively fast. Rapid peracetic acid formation can be best obtained in the presence of a strong acid catalyst like sulfuric acid.

In the 1st Stage Oxidizer, the bulk of the organosulfur compounds are converted to sulfones. Approximately 98 percent (96 to 99) conversion may be obtained in a residence time of 20 (5 to 30) minutes. The reactor pressure is not particularly limited, and may be selected according to need. The reactor may be suitably operated under adiabatic conditions at pressures ranging from atmospheric (14.7 psia) to 1500 psia. This range includes all values and subranges therebetween, including 14.7, 15, 17, 19, 25, 35, 50, 60, 70, 80, 90, 100, 250, 500, 750, 1000, 1250, 1500, and any combination thereof as appropriate. Most unit operations are carried out at or slightly above atmospheric pressure. The two liquid phases may suitably flow cocurrently upward through the reactor. As the reaction proceeds, the exothermic heat of oxidation causes the temperature of the reaction mixture to increase. An outlet temperature of approximately 181 °F (145 to 200) is expected. The 1st stage oxidizer must provide enhanced contacting between the two liquid phases. Mass transfer of peracetic acid from the heavy phase to the light phase is crucial to the overall reaction rate.

The reaction mixture that leaves the 1st Stage Oxidizer is fed to the 1st Stage Oxidizer Oil Decanter (V-1122) where the two liquid phases are separated by gravity settling. This decanter operates at 17 psia. The light phase is mostly hydrocarbon and acetic acid. This phase also contains sulfones and approximately 100 ppm_w sulfur in the form of unoxidized thiophenics. The heavy phase preferably includes mostly acetic acid and water. This phase also contains sulfuric acid, sulfones, and some hydrocarbon. Due to the extended time at elevated temperatures, the amount of active oxygen either in the form of hydrogen peroxide or in the form of peracetic acid is expected to be close to zero in both phases.

The light phase is pumped by P-1123 to the 2nd Stage Oxidizer (R-1140). The heavy phase is fed forward by gravity to the Water Flash Vessel (V-1160)

In the Water Flash Vessel (V-1160), a portion of the heavy phase from the outlet of the 1st Stage Oxidizer is vaporized and sent as a vapor to the Solvent Purification Column (T-1450). The Water Flash Vessel operates at 18 psia. The heat required for vaporization is supplied by the Water Flash Vessel Reboiler (X-1161) in the form of 150-psig (150 to 300) steam. Vaporization is conducted at 18 psia and 249 °F (240 to 410). The resulting vapor stream is mostly acetic acid with a water content of approximately 9 wt% (2 to 20). The liquid remaining after vaporization is primarily acetic acid, sulfones, and hydrocarbon with a small amount of water and approximately 2 wt% sulfuric acid. Most of this liquid is pumped by P-1162 to the inlet of the 2nd Stage Oxidizer. A portion is purged from the Oxidation System and sent to the Wastewater Neutralization Vessel (V-1710). The acetic acid lost in this stream represents approximately 43 percent of the overall acetic acid loss.

The water entering the system with the fresh hydrogen peroxide feed and the water generated within the system during the formation of peracetic acid is removed via partial vaporization of the heavy phase leaving the 1st stage reactor as described above. Although water generated during the formation of peracetic acid is primarily formed within the 2nd Stage Oxidizer, removal of this water from the Oxidation System can not be accomplished until after contact in the 1st Stage Oxidizer. The high temperatures used for vaporization would cause rapid and total decomposition of the active oxygen.

The sulfuric acid used to catalyze the formation of peracetic acid is theoretically unused during the reaction sequence. Therefore, total recycle of the sulfuric acid catalyst is theoretically possible. However, the fresh hydrogen peroxide entering the Oxidation System contains stabilizers in the form of non-volatile salts. These salts are soluble in water and tend to remain in the heavy phase circulating in the Oxidation System. Total recirculation of the heavy phase, after water removal via vaporization, would therefore result in an unchecked accumulation of the stabilizers. A heavy phase purge is therefore required to limit the accumulation of stabilizers. Unfortunately, this heavy phase purge also results in a loss of sulfuric acid from the Oxidation System. Therefore, fresh sulfuric acid must be added to negate these sulfuric acid losses, and any losses due to side reactions of sulfuric acid.

The gas oil feed to the 2nd Stage Oxidizer is first cooled to 130 °F (122 to 158) so that the combined feed will be 140 °F. Fresh stabilized 70-wt% hydrogen peroxide from storage and fresh 98 wt% sulfuric acid from a pipeline is added to the gas oil feed. In addition, heavy phase is fed forward from the Water Flash Vessel to the inlet of the 2nd Stage Oxidizer.

In the 2nd Stage Oxidizer, the fresh hydrogen peroxide is partially converted to peracetic acid and most of the unoxidized thiophenic compounds in the feed are converted to sulfones. Approximately 90 percent (88 to 95) conversion is obtained in a residence time of 20 (15 to 80) minutes. The reactor operates under adiabatic conditions at a pressure of 17 psia. The two liquid phases move cocurrently in a pipe flow reactor. The temperature rise in this reactor is expected to be near zero, since the heat of reaction for the formation of peracetic acid is very small and the amount of oxidation compared to the total mass flow is also very small. The 2nd Stage Oxidizer must also provide enhanced contacting between the two liquid phases. Mass transfer of peracetic acid from the heavy phase to the light phase is again crucial to the overall reaction rate.

The reaction mixture that leaves the 2nd Stage Oxidizer is fed to the 2nd Stage Oxidizer Oil Decanter (V-1141) where the two liquid phases are separated by gravity settling. This decanter operates at 17 psia. The light phase is mostly hydrocarbon and acetic acid. This phase also contains peracetic acid, sulfones and approximately 10 ppm_w of unoxidized thiophenics. The heavy phase preferably includes mostly acetic acid and water. This phase also contains hydrogen peroxide, peracetic acid, sulfuric acid, sulfones, and some hydrocarbon.

Efficient use of oxidant is accomplished by first feeding fresh oxidant to the 2nd Stage Oxidizer and then recycling the unused oxidant from the outlet of the 2nd Stage Oxidizer to the inlet of the 1st Stage Oxidizer. This flow path for the oxidant provides a high concentration of active oxygen in the 2nd Stage Oxidizer where the concentration of unoxidized organosulfur compounds is very low. The 2nd Stage Oxidizer operates at low temperature to minimize the consumption of oxidant in undesirable side reactions. Therefore, the heavy phase leaving the 2nd Stage Oxidizer contains a substantial amount of unused oxidant. This makes the heavy phase from the 2nd Stage Oxidizer an ideal candidate for recycle.

The light phase from the 2nd Stage Oxidizer Oil Decanter (V-1141) is fed via gravity to the Sulfox Extraction System. The heavy phase from the 2nd Stage Oxidizer Oil Decanter (V-1141) is recycled via P-1142 to the inlet of the 1st Stage Oxidizer.

Sulfox Extraction & Raffinate Washing (PFD 003-20-211-1210)

In Sulfox Extraction & Raffinate Washing, the small amounts of oxidant are removed from the raffinate by heat treatment and then most of the organosulfur compounds and acetic acid are removed from the gas oil via liquid-liquid extraction. Besides the gas oil fed forward from the Oxidation System, the recovered gas oil from the Solvent Purification System and the Hydrocarbon Recovery System are also treated in this system. The gas oil leaving this system contains 50 ppm_w of sulfur and 6000 ppm_w of acetic acid.

The Sulfox Extraction & Raffinate Washing System utilizes a stirred tank reactor (R-1210), a packed extraction column (T-1230), and a mechanical extraction column (T-1250). Gas oil hold up is provided at the end of this system by a simple vertical vessel (V-1280).

Fresh gas oil enters this system at 140 °F (122 to 158) from the Oxidation System via gravity from the 2nd Stage Oxidizer Oil Decanter (V-1141). Prior to entering the Destruct Reactor (R-1210), the gas oil is heated in X-1212 by interchanging heat with the discharge stream from the Destruct Reactor and in X-1213 by interchanging heat with the recycle solvent stream from the Solvent Recovery / Solvent Purification System. This heat recovery system raises the temperature of the gas oil to the desired Destruct Reactor temperature of 230 °F (212 to 250).

In the Destruct Reactor, any small amounts of oxidant are decomposed to oxygen and acetic acid. The residence time in the reactor is 10 minutes (5 to 20). An agitator is provided to maintain a homogeneous mixture. For startup purposes, the Destruct Reactor is equipped with a jacket serviced by 150 psig steam. Under steady state conditions, steam heating is not required.

The gas oil leaving the Destruct Reactor is pumped by P-1214 to the Sulfox Extraction Column (T-1230). Before entering the extraction column, the gas oil is cooled in X-1212 by interchanging heat with the feed

stream to the Destruct Reactor, in X-1233 by interchanging heat with the extract stream from the Sulfox Extraction Column, and finally in X-1234 by cooling water.

The solvent used in the Sulfox Extraction Column is a combination of crude acetic acid from the Solvent Flash Vessel (V-1410) and clean acetic acid from the bottom of the Solvent Purification Column (T-1450). This combined solvent is cooled to extraction temperature in X-1213 by interchanging heat with the feed stream to the Destruct Reactor, in X-1231 by interchanging heat with the extract stream from the Sulfox Extraction Column, and finally in X-1232 by cooling water.

In the Sulfox Extraction Column, more than 99 percent of the sulfones are removed from the gas oil.

There are three preferred process parameters associated with the Sulfox Extraction Column. These are extraction temperature, water content of the extraction solvent, and the solvent to feed ratio. The current design is based on an extraction temperature of 113 °F (100 to 150), solvent water content of 0.6 wt% (0.4 to 3.0), and a solvent to feed ratio of 1.25 (1.0 to 2.0). The optimum set of parameters for this extraction column must still be determined.

Higher extraction temperatures and higher solvent-to-feed ratios favor the removal of sulfones. Increased sulfone removal results in a smaller Raffinate Polishing System. Unfortunately, these same higher temperatures and higher solvent to feed ratios simultaneously increase the amount of hydrocarbons that are removed from the gas oil, thereby reducing yield in this system and increasing the capacity of the Hydrocarbon Recovery System. In addition, higher solvent-to-feed ratios also increase the capacity and energy requirements of the solvent recovery system. Lower temperatures are undesirable since special utility fluids such as chilled water would be necessary for cooling the feeds to the extraction column.

Higher water content decreases the amount of hydrocarbon extracted from the gas oil, thereby decreasing the amount of hydrocarbon processed in the Hydrocarbon Recovery System. However, the effect of water content on the ability of the solvent to extract sulfones must be researched further.

The extract leaving the bottom of the Sulfox Extraction Column is pumped by P-1235 to the Solvent Flash / Solvent Purification System. Before leaving the Sulfox Extraction & Raffinate Washing System, this relatively cold stream is used to cool the gas oil feed and the solvent feed to the Sulfox Extraction Column.

The raffinate leaving the top of the Sulfox Extraction Column is combined with the recovered hydrocarbon streams from the Solvent Purification System and the Hydrocarbon Recovery System. In addition, the gas oil used to rinse acetic acid the adsorption beds in the Raffinate Polishing System is also added to this stream.

The combined gas oil from the Sulfox Extraction Column, the Solvent Recovery System, the Hydrocarbon Recovery System and the Raffinate Polishing System is fed to the bottom of the Raffinate Wash Column (T-1250). This gas oil feed contains acetic acid that must be removed.

In the Raffinate Wash Column, most of the acetic acid is removed from the gas oil by washing with essentially pure water. This wash water is recycled from the Solvent Purification System and contains approximately 1.5 wt% acetic acid.

There is one preferred process parameter associated with the Raffinate Wash Column. This preferred parameter is the solvent to feed ratio. The current design is based on a solvent to feed ratio of 0.05 (0.025 to 0.1). Higher solvent to feed ratios result in higher acetic acid recovery. Unfortunately, this higher solvent flow will also result in higher energy requirements in the Solvent Purification System.

The washing temperature is 113 °F (100 to 125) and primarily depends on the temperature of the gas oil leaving the Sulfox Extraction Column.

The extract leaving the bottom of the Raffinate Wash Column is pumped by P-1252 to the Solvent Purification Column (T-1450) where the acetic acid is recovered and the water is purified for recycle.

The raffinate leaving the top of the Raffinate Wash Column flows via gravity to the Raffinate Hold Vessel (V-1280). This vessel provides 20 minutes of surge time. From the Raffinate Hold Vessel, the gas oil is pumped by P-1282 to the Raffinate Polishing System.

Raffinate Polishing (PFD 003-20-211-1310)

In the Raffinate Polishing System, small amounts of sulfur containing compounds and small amounts of acetic acid are removed by adsorption onto a solid bed adsorbent. The sulfur content of the gas oil is reduced to 10 ppm or less. It is estimated that the acetic acid content is reduced to 10 ppm or less.

It is possible to use refinery clay, also known as Fuller's Earth as an absorbent, but other absorbents may also be suitably used.

The Raffinate Polishing System utilizes two parallel adsorption columns (T-1310 & T-1320), one holding tank (S-1330), and two holding vessels (V-1350 & V-1360). One of the adsorption columns is polishing the gas oil while the other adsorption column is being regenerated. The overall cycle is 12 hours.

Gas oil from the Raffinate Holding Vessel (V-1280) is fed to one of the Raffinate Polishing Columns (T-1310). Organosulfur compounds and acetic acid are adsorbed onto the solid bed as the gas oil flows downward

through the column for a 6-hour period. Upon exiting the column, the purified gas oil flows via gravity to the Product Hold Tank (S-1330). After checking the quality, the gas oil is pumped intermittently by P-1331 to OSBL storage.

During the same time period, the other Raffinate Polishing Column (T-1320) is being regenerated. First, clean recycled acetic acid from the Solvent Hold Tank (S-1720) is pumped by P-1721 upward through the bed. Organosulfur compounds left on the solid bed adsorbent by the crude gas oil are now desorbed by the acetic acid. Upon exiting the top of the column, the spent acetic acid flows to the Spent Acetic Acid Hold Vessel (V-1350). This operation requires 3 hours. Then, desulfurized gas oil from the Product Hold Tank (S-1330) is pumped by P-1331 upward through the bed. The clean gas oil desorbs acetic acid left on the bed from the previous step. Upon exiting the top of the column, the spent gas oil flows to the Spent Gas Oil Hold Vessel (V-1360). This operation also requires 3 hours.

The spent acetic acid in the Spent Acetic Acid Hold Vessel is continuously pumped by P-1351 to the Solvent Flash & Solvent Purification System where the acetic acid is recovered and the organosulfur compounds removed from the gas oil via adsorption join the balance of the sulfur extract. The spent gas oil in the Spent Gas Oil Hold Vessel is continuously pumped by P-1561 to the Sulfox Extraction Column and Raffinate Wash System where the acetic acid and gas oil are recovered.

Solvent Flash & Solvent Purification (PFD 003-20-211-1410)

In the Solvent Flash System, the bulk of the acetic acid is separated from the sulfur extract for immediate recycle. In the Solvent Purification System, mixtures of acetic acid, water, and hydrocarbons from several sources within the process are purified for recycle and purging.

The Solvent Flash & Solvent Purification System utilizes a single stage flash (V-1410, X-1411, X-1420, and V-1421) and a packed distillation column (T-1450, X-1451, X-1460, and V-1461).

The extract from the bottom of the Sulfox Extraction Column (T-1230) and the spent acetic acid from the Spent Acetic Acid Hold Vessel (T-1350) are fed to the Solvent Flash Vessel (V-1410). The Solvent Flash Vessel Reboiler (X-1411) is used to vaporize a large portion of the feed with 300-psig steam.

The resulting bottoms stream which contains the sulfur extract and approximately 15 wt% (10 to 50) acetic acid is sent forward to the Solvent Recovery & Hydrocarbon Recovery System.

The flashed vapor is condensed in the Solvent Flash Vessel Overhead Condenser (X-1420) and then flows via gravity to the Solvent Flash Vessel Distillate Receiver (V-1421). The condensed distillate is mostly acetic

acid with 7-wt% (3 to 12) hydrocarbon. This hydrocarbon is mostly light boiling aliphatic and aromatic compounds that form minimum boiling homogeneous azeotropes with acetic acid.

The Solvent Flash System operates at approximately 45 psia (17 to 75). An elevated pressure is utilized to establish a higher condensing temperature in the Solvent Flash Vessel Overhead Condenser. This elevated temperature allows heat integration with the bottoms of the Solvent Purification Column (T-1450) by providing most of the reboiler heat duty required.

The condensed liquid from the Solvent Flash Vessel Overhead Condenser flows via gravity to the Solvent Flash Vessel Distillate Receiver (V-1421). This vessel provides approximately 15 minutes of surge capacity for the unit operations that receive recycle solvent. In addition, this vessel is used to monitor the acetic acid inventory within the process unit. Utilizing on/off level control, fresh acetic acid from storage is added to this vessel periodically to make up for acetic acid losses from streams leaving the process.

The crude acetic acid from this vessel is pumped by P-1422 to the 1st Stage Oxidizer (R-1120), to the Sulfox Extraction Column (T-1230), and to the Solvent Purification Column (T-1450). The streams flowing to R-1120 and T-1230 are recycle streams, while the stream to T-1450 acts as the hydrocarbon purge for the main solvent recycle loops. Without the purge stream to the Solvent Purification Column, azeotropic hydrocarbon accumulation would remain unchecked in this recycle loop causing potential problems in the Oxidation System and in the Sulfox Extraction System. Currently, the material balance is based on a recycle-to-purge weight ratio of 5.0 (4 to 10). At this recycle to purge ratio, the hydrocarbon composition in the crude acetic acid recycle loop is approximately 7.0 wt%. A higher recycle-to-purge ratio results in some energy savings in the Solvent Purification Column. However, this higher recycle-to-purge ratio also causes a higher hydrocarbon concentration in the recycle streams. The optimum recycle-to-purge ratio must still be determined.

The Solvent Purification Column (T-1450) receives vapor feed from the Water Flash Vessel (V-1160), liquid feed from the Raffinate Wash Column (T-1250), and liquid feed from the Solvent Flash Vessel Distillate Receiver (V-1421). Currently, each feed stream is introduced to the column at the optimum feed location based on each individual feed stream composition. There are two feed locations. The column operates at 17 psia. In the lower portion of this distillation column, water and light hydrocarbons are stripped from acetic acid. In the upper portion of this distillation column, acetic acid is removed from water and hydrocarbon. The separation accomplished in this column is relatively difficult since the relative volatility between water and acetic acid is low. The heat and material balance for this column is currently based on a reflux ratio of 3.8 by weight and a total of 38 theoretical stages. The optimum configuration and operating conditions of this column must still be determined.

Approximately 90 percent of the heat required by the Solvent Purification Column is supplied by the Solvent Flash Vessel Overhead Condenser (X-1420). Due to layout considerations, forced circulation is utilized for this reboiler. This arrangement allows the liquid condensate on the hot side of this reboiler to flow via gravity to the Solvent Flash Vessel Distillate Receiver (V-1421). The balance of the heat requirement for the Solvent Purification Column is supplied in the Solvent Purification Column Trim Reboiler (X-1451) by 150-psig steam. This is a thermosiphon reboiler and is used to control the water content of the streams leaving the bottom of the column.

The streams leaving the bottom of the Solvent Purification Column are pumped by P-1452 and contain mostly acetic acid with approximately 0.5 wt% water and 1.5 wt% hydrocarbon. The largest of the streams is internally recycled to the main reboiler. The other two streams represent the net bottoms output from the distillation column. One of these streams is recycled to the Sulfox Extraction Column (T-1230). The other stream is sent to the Solvent Hold Tank (S-1720) where it becomes the recycle stream used to regenerate the adsorption beds in the Raffinate Polishing System.

Most of the hydrocarbon and water in the feeds to the Solvent Purification Column are driven overhead. At the top of the column, overhead vapors are condensed in the Solvent Purification Column Overhead Condenser (X-1460). This is a total condenser utilizing cooling tower water as a heat sink. It may be desirable to vent non-condensable gases formed in the Water Flash Vessel by the decomposition of active oxygen containing species. Since the light hydrocarbons and water form minimum boiling heterogeneous azeotropes, two liquid phases are formed upon condensation. The immiscibility in this condensed stream is due to the high concentrations of water present. The two liquid phases are separated by gravity settling in the Solvent Purification Column Reflux Decanter (V-1461).

The light phase contains 99.6 wt% hydrocarbon and is recycled via gravity to the bottom of the Raffinate Wash Column (T-1250) where the recovered azeotropic hydrocarbon joins the main gas oil stream. The heavy phase which is water rich and contains approximately 1.4 wt% acetic acid is pumped by P-1462 to the Solvent Purification Column as reflux, to the top of the Raffinate Wash Column (T-1250) as wash water recycle, and the Wastewater Neutralization Vessel (V-1710) as purge. The recycle water to the Raffinate Wash Column is cooled in the Solvent Purification Column Water Distillate Cooler (X-1463) by cooling tower water. The purge stream leaving this distillation column represents most the water fed to the Oxidation System with the fresh hydrogen peroxide feed and most of the water formed by reaction in the Oxidation System. The acetic acid leaving in this stream represents approximately 30 percent of the total acetic acid losses.

Solvent Recovery & Hydrocarbon Recovery (PFD 003-20-211-1510)

In the Solvent Recovery System, additional acetic acid is separated from the sulfur-rich extract for recycle. In the Hydrocarbon Recovery System, the remaining acetic acid and a large portion of the hydrocarbons in the sulfur-rich extract are recovered for recycle.

The Solvent Recovery & Hydrocarbon Recovery System utilizes a relatively small packed distillation column (T-1510, X-1511, X-1520, and V-1521) operating at atmospheric pressure and a relatively large packed distillation column (T-1550, X-1551, X-1560, V-1561, and X-1563) operating under vacuum. Vacuum is generated by the Hydrocarbon Recovery Column Vacuum System (Z-1570), which is a steam jet package. Condensate from the vacuum system is processed through the Wastewater Neutralization Vessel (V-1710), which acts simultaneously as the seal for the vacuum system barometric legs and as the neutralization point for all wastewater streams leaving the process.

The Solvent Recovery Column (T-1510) receives the sulfur extract stream from the bottom of the Solvent Flash Vessel (V-1410). This stream contains hydrocarbons, approximately 7.3 wt% sulfones and 15 wt% acetic acid. Above the feed point of the distillation column, hydrocarbon is removed from acetic acid. Below the feed point of the distillation column, acetic acid is stripped from the hydrocarbons and the sulfones. The separation accomplished in this column is relatively easy since the relative volatility between acetic acid and hydrocarbons is high. The heat and material balance for this column is currently based on a reflux ratio of 0.5 by weight and a total of 8 theoretical stages. The optimum configuration and operating conditions of this column must still be determined.

Approximately 88 percent of the acetic acid in the feed to the Solvent Recovery Column is sent overhead. Some hydrocarbon and essentially all the water in the feed is also sent overhead. The atmospheric bubble point of the liquid stream leaving the bottom of the distillation column limits additional recovery of acetic acid.

At the top of the column, overhead vapors are condensed in the Solvent Recovery Column Overhead Condenser (X-1520). This is a total condenser utilizing cooling tower water as a heat sink. The condensed liquid flows to the Solvent Recovery Column Reflux Drum (V-1521), which provides approximately 7.5 minutes of liquid surge capacity. The liquid leaving the Solvent Recovery Column Reflux Drum is pumped by P-1522 to the top of the Solvent Recovery Column as reflux and to the Solvent Flash Vessel Distillate Receiver as recycle.

The heat required by the Solvent Recovery Column is supplied in the Solvent Recovery Column Reboiler (X-1511) by 300 psig steam. Forced circulation is used for this reboiler since there is a significant increase in the bubble point of the liquid as vaporization occurs. The net liquid leaving the bottom of the column is pumped by P-1512 to the Hydrocarbon Recovery Column (T-1550). This stream is mostly hydrocarbon and contains approximately 2 wt% acetic acid and 8 wt% sulfones.

The Hydrocarbon Recovery Column (T-1550) receives the sulfur-laden stream from the bottom of the Solvent Recovery Column (T-1510). Above the feed point of the distillation column, sulfones are removed from acetic acid and hydrocarbons. Below the feed point of the distillation column, acetic acid and hydrocarbon are stripped from the sulfones. The heat and material balance for this column is currently based on a reflux ratio of 0.15 by weight and a total of 8 theoretical stages. The optimum configuration of this column must still be determined.

The top of the Hydrocarbon Recovery Column (T-1550) operates at an absolute pressure of 10 mmHg. The bottom of this column operates at an absolute pressure of 15 mmHg. The pressures utilized in this column were chosen based on a balance between the complexity of the vacuum system, the recovery of hydrocarbon overhead, and the bubble point of the resulting bottom stream. The current configuration results in a column hydrocarbon recovery of 80 percent by weight, which increases the overall hydrocarbon recovery for the entire process to 90 percent by weight.

At the top of the column, overhead vapors are condensed in the Hydrocarbon Recovery Column Overhead Condenser (X-1560) and the Hydrocarbon Recovery Column Vent Condenser (X-1563). The main condenser utilizes cooling tower water, while the vent condenser utilizes 25 wt% ethylene glycol at 10 °F. The vent condenser minimizes losses of acetic acid to the vacuum system. The liquid from both condensers flows to the Hydrocarbon Recovery Column Reflux Drum (V-1561), which provides approximately 7.5 minutes of liquid surge capacity. The liquid leaving the Hydrocarbon Recovery Column Reflux Drum is pumped by P-1562 to the top of the Hydrocarbon Recovery Column as reflux and to the bottom of the Raffinate Wash Column (T-1250) as recovered hydrocarbon and acetic acid.

The heat required by the Hydrocarbon Recovery Column is supplied in the Hydrocarbon Recovery Column Reboiler (X-1551) by 300-psig steam. A falling film reboiler is used for this application due to the potential thermal sensitivity of the bottom product. The net liquid leaving the bottom of the column is pumped by P-1552 through the Hydrocarbon Recovery Column Bottoms Cooler to storage. This stream contains approximately 68 wt% hydrocarbon and 32 wt% sulfones.

The vapor leaving the column vent condenser flows to Hydrocarbon Recovery Column Vacuum System (Z-1570), which is a three-stage vacuum package utilizing 150-psig steam as the motive fluid and preferably including 3 jets (Y-1570, Y-1573, and Y-1576) and 3 after-condensers (X-1571, X-1574, and X-1577). The net gas leaving the vacuum system is sent to offgas treatment. Very little acetic acid is lost in this stream. The condensed process liquid and condensed steam from each after condenser flows via gravity through two separate barometric legs and a separate atmospheric leg to the Wastewater Neutralization Vessel (V-1710). The acetic acid lost in this stream represents approximately 26 percent of the overall acetic acid loss.

The Wastewater Neutralization Vessel receives feed from the Water Flash Vessel (V-1160) in the Oxidation System, from the Solvent Purification Column Reflux Decanter (V-1461) in the Solvent Purification System, and the Hydrocarbon Recovery Column Vacuum System (Z-1570). These streams contain sulfuric acid and/or acetic acid which must be neutralized before purging to a wastewater treatment system. The neutralization is accomplished by feeding 25 wt% caustic to this vessel. Any sulfuric acid is converted to sodium sulfate and any acetic acid is converted to sodium acetate. The sensible heat in the warm feed streams and the heat of neutralization is removed by recirculation through the Wastewater Neutralization Vessel Cooler (X-1711), which is serviced by cooling tower water. The net wastewater leaving the Wastewater Neutralization Vessel is pumped by P-1712 to wastewater treatment.

Some preferred embodiments, dimensions and design characteristics are summarized in the equipment list given in Appendix D.

Reactors

Preferably, there are three reactors in the invention process. These are the 1st Stage Oxidizer (R-1120), the 2nd Stage Oxidizer (R-1140), and the Destruct Reactor (R-1210).

For the 1st Stage Oxidizer, a mechanically agitated reciprocating plate contactor (Karr Column) may be suitably used, although any type of reactor may be employed. Normally, this type of contactor is used in countercurrent liquid-liquid extraction. This device may be preferably utilized as a cocurrent upflow liquid-liquid contactor. With this flow pattern, this device mimics the effects of a plug flow reactor with minimal back mixing. The agitation provided by the perforated reciprocating plates enhances mass transfer by creating dispersed heavy phase droplets within the continuous light phase. In addition, the agitation minimizes the difference in the velocity of the phases in order to give approximately equal residence time for each phase.

A pilot scale Karr Column achieved approximately 96 percent conversion of the sulfur containing compounds in the gas oil. The volume of the commercial Karr Column is based on the 20-minute residence time used in the test apparatus and the dimensions were scaled according to the hydraulic capacity of the test apparatus. The commercial scale Karr Column utilizes 140 perforated plates.

Utilizing a Karr Column for the 1st Stage Oxidizer is a very expensive option. In addition, this apparatus is generally speaking unattractive to operating personnel due its mechanical nature and probable need for intensive maintenance. There are potential process improvements aimed at replacing this apparatus with a less expensive type without moving parts.

The 2nd Stage Oxidizer is preferably a pipe reactor, and may optionally be packed with static mixer elements. The volume of the reactor is based on the 10-minute residence time used in the laboratory experiments. The

diameter of the pipe is based on the minimum velocity necessary for creating coarse heavy phase droplets that are dispersed in the continuous light phase.

For the Destruct Reactor, a continuous stirred vessel was chosen. The operating temperature is 230 °F. During steady state operation, interchangers transfer sufficient heat to the feed from other process streams. A conventional jacket is preferably provided for startup purposes and uses 150 psig steam when heating is necessary. The working liquid volume provides approximately 10 minutes of residence time. The dimensions were chosen for maximizing agitator performance.

Extraction Columns

Preferably, there are two liquid-liquid extraction columns in the invention process. These are the Sulfox Extraction Column (T-1230) and the Raffinate Wash Column (T-1250).

The Sulfox Extraction Column is a countercurrent packed bed liquid-liquid contactor. The column is equipped with SMVP structured packing.

The Raffinate Wash Column is a Scheibel extractor or a countercurrent mechanically agitated liquid-liquid contactor. During the same testing program, the trials utilizing a packed bed extractor in this application revealed poor dispersion of the phases. Additional energy input is desirable to overcome the high interfacial surface tension between the two liquid phases. As stated earlier, the solvent to feed ratio in this column is very low. This low solvent to feed ratio also decreases the mass transfer efficiency. The commercial column was scaled from the pilot tests based on the hydraulic capacity needed for the larger throughput. The commercial column contains 36 agitated stages. The heavy phase is dispersed, while the light phase is continuous.

Utilizing a Scheibel Extractor for the Raffinate Wash Column is a very expensive option. In addition, this apparatus is generally speaking unattractive to operating personnel due its mechanical nature and probable need for intensive maintenance. It is also possible to replace this apparatus with a less expensive type without moving parts.

Distillation Columns

Preferably, there are three distillation columns in the invention process. These are the Solvent Purification Column (T-1450), the Solvent Recovery Column (T-1510), and the Hydrocarbon Recovery Column (T-1550). In all three cases, conventional packed columns were utilized.

The Solvent Purification Column is relatively large with an estimated height of 82 feet (tangent to tangent) and a diameter of 7 feet. The separation is difficult due to the low relative volatility between water and acetic acid. A total of 38 theoretical stages are preferred in view of separation completeness. High efficiency packing is utilized to minimize the column height. The column operates slightly above atmospheric pressure at 17 psia. The column includes three packed sections so that the optimum feed location is used for the various streams entering the column.

The Solvent Recovery Column is relatively small with an estimated height of 25 feet (tangent to tangent) and a diameter of 18 inches. The separation of acetic acid from extract is relatively easy. A total of 8 theoretical stages are preferred in view of separation completeness. Standard packing is utilized to minimize cost. The column operates slightly above atmospheric pressure at 18 psia.

The Hydrocarbon Recovery Column is relatively short with an estimated height of 28 feet (tangent to tangent) but has a relatively large diameter at 7 feet. The separation of hydrocarbons from sulfones is relatively easy. However, the column operates at a pressure of 0.19 psia, which creates considerable volumetric vapor traffic. A total of 8 theoretical stages are preferred in view of separation completeness. Standard packing is utilized to minimize cost.

Liquid-Liquid Decanters

Preferably, there are three decanters in the invention process. These are the 1st Stage Oxidizer Oil Decanter (V-1122), the 2nd Stage Oxidizer Oil Decanter (V-1141), and the Solvent Purification Column Reflux Decanter (V-1461).

Conventional horizontal gravity separators with internal baffles are utilized. Generally speaking, the materials being separated have a low viscosity (< 2 cP) and the density ratio between the heavy phases and light phases are approximately 1.2. Therefore, separations are relatively easy. Conservative methods were utilized for sizing, and therefore, a reduction in the dimensions of these decanters is definitely possible.

Efficient separation in the 2nd Stage Oxidizer Oil Decanter is preferred since carryover of heavy phase to the Destruct Reactor (R-1210) would compromise its 316 SS materials of construction.

Vapor-Liquid Separators

Preferably, there are five vapor-liquid separators in the invention process. These are the Water Flash Vessel (V-1160), the Solvent Flash Vessel (V-1410), the Non-Oxygen Containing Offgas Knockout Vessel (V-1740), the Oxygen Containing Offgas Knockout Vessel (V-1745), and the Emergency Relief System Knockout Vessel (V-1780). Two of these five vapor-liquid separators are shown on the five Process Flow Diagrams,

the Water Flash Vessel and the Solvent Flash Vessel. The other three vapor-liquid separators are only included in the equipment list and the general arrangements.

The Water Flash Vessel and the Solvent Flash Vessel are conventional vertical separators with mist eliminators. Generally speaking, the vapor-liquid separation in these vessels is relatively easy. Efficient separation in the Water Flash Vessel is preferred since carryover of the liquid phase to the Solvent Purification Column (T-1450) would compromise its 316 SS materials of construction.

The Non-Oxygen Containing Offgas Knockout Vessel, the Oxygen Containing Offgas Knockout Vessel, and the Emergency Relief System Knockout Vessel are included in the design to provide liquid free vapor streams at the battery limits of the process.

Adsorption Columns

Preferably, there are two adsorption columns in the invention process. These are the Raffinate Polishing Columns (T-1310 & T-1320). The columns are identical with an estimated height of 42 feet (tangent to tangent) and a diameter of 5 feet. Each column contains two 15-foot beds of refiner's clay. Both columns are used for polishing the gas oil by removing small amounts of sulfur-containing compounds and small amounts of acetic acid.

Heat Exchangers

Preferably, there are a total of 25 heat exchangers in the invention process. Shell & Tube exchangers are utilized in all cases. Generally speaking, a horizontal orientation was used for condensing applications and a vertical orientation was used for vaporizing applications.

There are five traditional reboilers. The Water Flash Vessel Reboiler (X-1161), the Solvent Flash Vessel Reboiler (X-1411), and the Solvent Purification Column Trim Reboiler (X-1451) are thermosiphons. The Solvent Recovery Column Reboiler (X-1511) utilizes forced circulation since bubble point variation along the boiling path is large. The Hydrocarbon Recovery Column Reboiler (X-1551) is based on falling film technology to minimize the hot wall contact time for the concentrated sulfone stream.

The Solvent Flash vessel Overhead Condenser (X-1420) has a dual function. The exchanger is used to condense vapors from the Solvent Flash Vessel while vaporizing liquid from the Solvent Purification Column. A vertical orientation is utilized with the vaporization on the tube side and the condensation on the shell side. Forced circulation is utilized on the vaporizing tube side to allow gravity flow liquid return to the Solvent Flash Vessel Distillate Receiver for the condensing shell side.

If present, non-condensable gases do not create a problem in the condensers.

Storage Tanks

Three storage tanks are preferably used in the invention process. These are the Hydrogen Peroxide Storage Tank (S-1040), the Product Hold Tank (S-1330), and the Solvent Hold Tank (S-1720). All three tanks are API type containers.

The Hydrogen Peroxide Storage Tank is a nominal 24,000 gallons. The size is based on obtaining a 10,000-gallon delivery every three days and provides a hold-up volume just over 3 days at design capacity. This tank should be equipped with emergency dilution water and an emergency deluge system.

The Product Hold Tank is a nominal 42,000-gallon. This size provides just over 4 hours of product holdup.

The Solvent Hold tank is a nominal 24,000-gallon. This tank is sized to hold the inventory of acetic acid within the process unit.

Pumps

Preferably, there are a total of 41 pumps in the invention process. Most are seal-less horizontal centrifugal design. Several have double or single mechanical seals. There are three air diaphragm pumps. Pumps in continuous service are spared.

Equipment Materials of Construction

Most of the equipment in contact with process fluid in the invention process are constructed of 316 SS, standard (316) or low-carbon (316L), due to the presence of hot acetic acid.

In the oxidation section, the equipment is primarily constructed from Alloy 20 due to the presence of sulfuric acid in an aqueous/acetic acid solution at elevated temperature. The choice of Alloy 20 is based on experience with similar systems. However, this choice may be confirmed by corrosion testing of the compositions shown in the material balance at the operating temperatures of the process. If Alloy 20 is not suitable, Hastelloy C276 would almost certainly be sufficient. However, this choice will certainly increase the cost of the equipment in the oxidation system.

The Water Flash Vessel (V-1160) is constructed from glass-lined carbon steel. The tube side of the Water Flash Vessel Reboiler (X-1161) and the Water Flash Vessel Bottom Pump (P-1162) are constructed from

Hastelloy C276. These choices are based on the high concentration of sulfuric acid (~ 2 wt%) and elevated temperature (~250 °F) in this portion of the process.

The equipment that contacts acetic acid free gas oil and extract are constructed from carbon steel.

Equipment in contact with utility fluids and off-line equipment are constructed from carbon steel.

This subsection includes a short description of a preferred equipment arrangement and the most preferred features of the process layout.

Plan views and elevations for the process structure are shown in Appendix E. The drawings included are Elevation 01, Elevation 02, Plan View @ Elevation 00', Plan View @ Elevation 20', Plan View @ Elevation 40', and Plan View @ Elevation 60'.

The ground floor is separated into four independent diked areas to provide fire zone isolation. The entire process structure is included in one diked area. A separate diked area holds the Product Hold Tank (S-1330) and the Solvent Hold Tank (S-1720). Two additional diked areas are provided for the Hydrogen Peroxide Storage Tank (S-1040) and the Emergency Relief System Knockout Vessel (V-1780).

The process area dike contains the main sump serviced by a large electrical pump. This primary pump delivers all rainwater to the battery limits upon operator permission. The other three diked areas contain secondary sumps serviced by air diaphragm pumps. With operator permission, these secondary pumps empty their respective diked area to the main sump for delivery to the battery limits.

The frame at the long center of the structure preferably includes five full height 25 foot by 20 foot bays that provide pipe ways for the main process and utility pipelines. On one side of this steel structure is five full height 25 foot by 25 foot process bays where the 1st Stage Oxidizer, the 1st Stage Oxidizer Decanter, the Adsorption Columns, the distillation column condensers and reflux drums, and many of the process surge vessels are located. On the other side of the pipe way is one full height 25 foot by 25 foot process bay where the 2nd Stage Oxidizer, the 2nd Stage Oxidizer Decanter, and the Destruct Reactor are located. In the remaining area, a steel frame is absent and equipment items located in these areas are free standing on skirts.

All pumps are located on the ground floor and straddle the area below the main pipe ways. This allows easy access for maintenance. Horizontal heat exchangers are oriented toward the outside of the steel structure to allow easy bundle removal.

The equipment items that operate liquid full are all located above the 25 foot elevation to avoid two phase relief during a fire scenario. These equipment items are the 1st Stage Oxidizer (R-1120), the 2nd Stage Oxidizer (R-1140), the Sulfox Extraction Column (T-1230), the Raffinate Wash Column (T-1250), and the two Adsorption Columns (T-1310 & T-1320).

Generally speaking, the positions for process equipment were chosen to take advantage of gravity flow and eliminate pumps where possible. Preferred gravity flow relationships are listed below:

- (1) The top of the 1st Stage Oxidizer (R-1120) is located above the 1st Stage Oxidizer Decanter (V-1122).
- (2) The 1st Stage Oxidizer Decanter (V-1122) is located above the Water Flash Vessel (V-1160).
- (3) The top of the 2nd Stage Oxidizer (R-1140) is located above the 2nd Stage Oxidizer Decanter (V-1141).
- (4) The 2nd Stage Oxidizer Decanter (V-1141) is located above the Destruct Reactor (R-1210).
- (5) The top of the Sulfox Extraction Column (T-1230) is located above the top of the Raffinate Wash Column (T-1250).
- (6) The top of the Raffinate Wash Column (T-1250) is located above the top of the Raffinate Hold Vessel (V-1280).
- (7) The Raffinate Polishing Columns (T-1310 & T-1320) are located above the Product Hold Tank (S-1330), the Spent Acetic Acid Hold Vessel (V-1350), and the Spent Gas Oil Hold Tank (V-1360).
- (8) The bottom of the Solvent Flash Vessel Overhead Condenser (X-1420) is simultaneously above the top of the Solvent Flash Vessel Distillate Receiver (V-1421) and the bottom of the Solvent Purification Column (T-1450). This is the reason for utilizing tube side forced circulation on X-1420 rather than natural circulation in the form of a thermosiphon reboiler.

The Hydrocarbon Recovery Column Vacuum System (Z-1570) is located on the third elevated floor to provide enough height for the barometric legs that extend down to the Wastewater Neutralization Vessel (V-1710).

The raw material and utility consumption for the invention was extracted from the balances shown on the Process Flow Diagrams in Appendix C1, the Material Balances shown in Appendix C2, and the Equipment List shown in Appendix D. A summary is shown in the table below.

Feed Materials			
	Usage	Units	Remarks
Hydrogen Peroxide (100%)	1020	lb/hr	Stream 1040-01
Acetic Acid (100%)	46	lb/hr	Stream 1110-08 Stream 1410-10 Stream 1510-06
Sulfuric Acid (100%)	0.9	lb/hr	Stream 1020-01
Sodium Hydroxide (100%)	31	lb/hr	Stream 1030-01
Utilities			
	Usage	Units	Remarks
Electric Power	143	kw	From Equipment List
Steam	47,007	lb/h	From PFD Heat Exchanger Duties
Cooling Water	5,312	gpm	From PFD Heat Exchanger Duties

The potential advantages include:

- (1) Two Stage Addition of Oxidant – This assures that the lowest concentrations of unoxidized sulfur compounds are in contact with the highest concentrations of oxidant.
- (2) Water Removal between Oxidation Stages – This allows recycle of the heavy phase leaving the 2nd stage oxidation to the 1st stage oxidation without loss of oxidant. This also eliminates any water dilution affects on the fresh oxidant added to the 2nd stage oxidation, and therefore, promotes maximum mass transfer of oxidant from the heavy phase to the light phase.
- (3) Second Stage Oxidation at Reduced Temperature – This minimizes the unwanted side reactions in the 2nd stage oxidation, and therefore, preserves the oxidant for recycle to the 1st stage oxidation.

Accordingly, and based on the Process Flow Diagrams in Appendix C1, extensive laboratory experimentation proved the viability and repeatability of the present process, and particularly the oxidation. The experiments consistently produced gas oil with a sulfur content less than 10 ppm by weight.

The residence time required for oxidation in the first stage is relatively short. Conversions greater than 98 percent were obtained in less than 5 to 10 minutes. However, the experimental data also indicated that a relatively long residence time is required in the 2nd stage oxidation. Long residence time in the 2nd stage oxidation results in a large expensive reactor. In addition, this long residence time may cause excessive depletion of oxidant via side reactions in the heavy phase.

Without wishing to be bound by theory, and based on measurements of the active oxygen concentration in the light phase during the 2nd stage oxidation, it is believed that the reaction mechanism at low concentrations of unoxidized sulfur compounds is kinetically controlled rather than mass transfer controlled. In addition, the present inventors found that the solubility of peracetic acid in the light phase is great enough to provide a stoichiometric excess for completing the oxidation.

An embodiment of a revised oxidation system is shown in Appendix G.

A two-stage oxidation with water removal between stages and a lower 2nd stage oxidation temperature is still employed. However, in this revised scheme, the 2nd Stage Oxidizer is a single liquid phase plug flow reactor. Mass transfer of the oxidant to the light phase is accomplished in a short residence time static mixer placed immediately up-stream of the single liquid phase plug flow reactor. A residence time of one to two minutes is sufficient to transfer sufficient oxidant from the heavy phase into the light phase. The lower portion of the plug flow reactor is used to separate the two phases via gravity settling. The heavy phase is immediately recycled to the 1st Stage Oxidizer. Immediate removal of the heavy phase minimizes the extent of side reactions, and therefore, maximizes the amount of recycle oxidant. The isolated light phase flows through the plug flow reactor, where residence times can be made arbitrarily long without an excessive cost impact.

Since the residence time in the 2nd Stage Oxidizer is shorter than the time required for sufficient in situ conversion of hydrogen peroxide to peracetic acid, a continuously stirred tank reactor (CSTR) is added to the oxidation system. The Peracetic Acid Reactor (R-1110) is used to pre-form the peracetic acid from fresh 70 wt% hydrogen peroxide and recycle acetic acid. The fresh catalyst used to replace the sulfuric acid purged from the oxidation system via Water Flash Vessel (V-1160) is introduced through the Peracetic Acid Reactor. Although a CSTR was chosen for the application, a simple plug flow reactor may also be employed. The CSTR is expected to cost more than the plug flow reactor, but it does offer an easier mode of operation, especially with respect to startup of the oxidation system.

Based on the short residence time requirements for the 1st stage oxidation, the relatively expensive, high maintenance Karr Column is replaced with a plug flow pipe reactor equipped with an internal static mixer. This is expected to reduce capital costs and maintenance costs.

One advantage of the process is that the overall degree of desulfurization is infinitely variable between 0 and 100% (either weight percent or molar percent). This range particularly includes 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100% and any combination thereof. For example, if a product stream containing 1000 ppm_w sulfur (or sulfur compounds) is desired, and the feed stream contains 2000 ppm_w sulfur (or compounds), then the process can be tuned to achieve an overall degree of desulfurization of 50%. In the oxidation system of the present process it may be preferable to achieve gas oil containing as little as 2-30 ppm_w unoxidized sulfur compounds. The continuous flow pilot testing results indicate that the oxidation system in the present process can consistently produce gas oil with less than 25 ppm_w of unoxidized sulfur compounds. These ranges include all values and subranges therebetween, including 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 16, 18, 20, 22, 24, 25, 28, and 30 ppm_w of unoxidized sulfur compounds.

To obtain gas oil with less than 10 ppm_w of unoxidized sulfur compounds (including 2, 3, 4, 5, 6, 7, 8, 9 and less than 10 ppm_w) a three-stage oxidation system may be suitably be used.

The residence time in the 2nd Stage Oxidizer shown on the Process Flow Diagram in Appendix G would be divided appropriately into two reactors. Each of these reactors would be equipped with a mixing zone at the inlet, followed by a separation zone where the heavy phase would be removed. Finally, each of these reactors would have a single liquid phase pipe flow segment where the sulfur containing compounds in the light phase continue to be oxidized.

The gas oil would flow through these two reactors in series. The fresh peracetic acid solution from the Peracetic Acid Reactor (R-1110) would be split into two parallel streams. Each of these two peracetic acid streams would be fed to the inlet mixing sections of the 2nd Stage Oxidizer and 3rd Stage Oxidizer. The heavy phase from the settling zone of each of these reactors would be recycled to the 1st Stage Oxidizer.

In the process described thus far, the spent acetic acid used to regenerate the Raffinate Polishing Columns is sent to the Solvent Recovery & Solvent Purification System (PFD 003-20-211-1410) Purification Column. This spent acetic acid contains sulfone compounds and possibly small amounts of unoxidized sulfur compounds. A more energy efficient approach is to recycle the spent acetic acid directly to the beginning of the process to partially saturate the gas oil feed. This reduces the heat load requirements for the Solvent Flash Vessel (V-1410) by approximately 10 percent. In addition, if the spent acetic acid from the Raffinate Polishing Columns contain unoxidized sulfur compounds, recycling this stream to the oxidation system would increase conversion and eliminate a potential buildup of these materials in this recycle loop.

Add an extraction column to the oxidation system where heavy phase from the discharge of the 1st Stage Oxidizer Oil Decanter (V-1122) is contacted with fresh gas oil. Acetic acid in the heavy phase will be extracted into the gas oil. This reduces the amount of acetic acid that must be vaporized in the Water Flash Vessel (V-1160), thereby reducing steam consumption. In addition, the amount of acetic acid processed through the Solvent Purification Column (T-1450) will be reduced. An added benefit could be the recovery of a portion of the unreacted peracetic acid leaving the 1st Stage Oxidizer.

In the current design, crude solvent from the Solvent Flash Vessel (V-1410) is used to saturate the fresh gas oil feed. This crude solvent contains a substantial amount (~ 4.4 wt%) of aromatic hydrocarbons. These aromatic hydrocarbons are susceptible to chemical attack by the oxidant, and therefore, could cause additional oxidant and gas oil losses. The acetic acid from the bottom of the Solvent Purification Column (T-1450) has a lower aromatic content (~ 1.1 wt%). Therefore, use the acetic acid from the bottom of the Solvent Purification Column to saturate the fresh gas oil feed and use all the crude acetic acid from the Solvent Flash Vessel for feeding the Sulfox Extraction Column (V-1230).

It is possible to use a liquid ring vacuum pump for the Hydrocarbon Recovery Column (T-1550) rather than a steam jet system. If fresh gas oil can be used as the vacuum pump cooling fluid, it may be possible to reduce the refrigeration requirements for the Chiller System (Z-1580) and simultaneously reduce the losses of acetic acid. Instead of utilizing 0 °F brine, 40 °F chilled water may be possible. Most preferably, the Chiller System (Z-1580) and the Hydrocarbon Column Vent Condenser (X-1563) are eliminated entirely. It is preferable that the gas oil absorbs the acetic acid from the vent stream. Once this acetic acid is absorbed, it can then be feed to the front of the process and recovered. Preferably, the maximum possible acetic acid recovery is 12.0 lb/hr, which is worth 0.028 USD per bbl of product. In addition, steam consumption and wastewater production is reduced. However, additional electricity is needed.

A Scheibel Column may be suitably utilized for the Raffinate Wash Column (T-1250). It is possible to replace the Scheibel Column with a series of mixer / settlers in order to reduce cost. With mixer / settlers, it may also be possible to decrease the wash water requirements.

If unoxidized thiophenes co-distill in the Hydrocarbon Recovery Column (T-1550), the recycle distillate should be sent to the oxidation system rather than the Raffinate Wash Column (T-1250).

It is possible to add a feed vaporizer to the Solvent Flash Vessel (V-1410) due to large difference in bubble points between feed and bottoms liquid.

It may be possible to delete the Solvent Recovery Column Reflux Drum (V-1521) and reflux the top of the Solvent Recovery Column (T-1510) directly from the Solvent Recovery Column Overhead Condenser (X-1521). It may also be possible to delete P-1522A/B.

It may be possible to delete the Destruct Reactor (R-1210). During the continuous flow pilot testing, the oxidant level leaving the 2nd stage oxidation was monitored. The concentration of active oxidant was very low. If the Destruct Reactor is removed, most of the active oxygen remaining in the gas oil should be removed in the Sulfox Extraction Column (T-1230) by the acetic acid extraction solvent. The solvent stream leaving the Sulfox Extraction Column flows to the Solvent Flash Vessel (V-1410) where the high temperature will certainly destroy any remaining active oxygen.

It is possible to add steam to the bottom of the Hydrocarbon Recovery Column (T-1550). This could allow a higher operating pressure and/or increased recovery of hydrocarbon.

There are currently five heat exchangers that cool process liquids with cooling water. These are: X-1232 (3.331 mmbtu/hr), X-1234 (1.216 mmbtu/hr), X-1463 (0.368 mmbtu/hr), X-1553 (0.819 mmbtu/hr), and X-1721 (0.857 mmbtu/hr). The heat duties for these five exchangers sum to a total load of 6.6 mmbtu/hr. This

is worth ~ 0.21 usd/bbl of feed or 0.23 usd/bbl of product. It may be possible to add one or more process/process interchangers to recover some of this wasted energy.

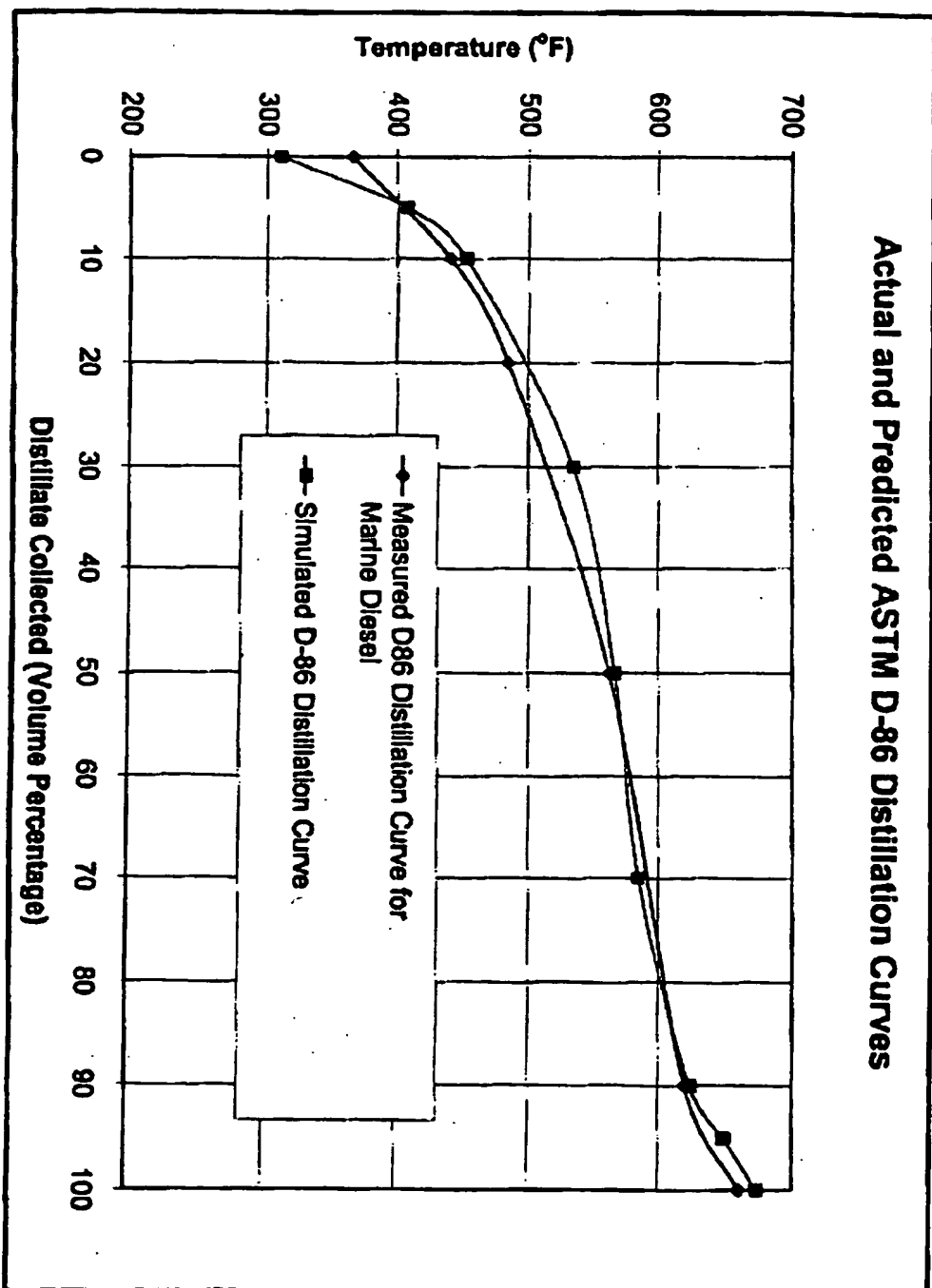
The Solvent Purification Column Overhead Condenser (X-1460) has a heat duty of 26.6 mmbtu/hr. It may be possible to recover a large portion of this energy by increasing the operating pressure of the Solvent Purification Column (T-1450). However, increasing this pressure would either increase the size of the Solvent Flash Vessel Reboiler (X-1411) or increase the steam pressure requirements for this exchanger.

The process may be suitably used for a gas oil sulfur content of 5100 ppm_w. However, it is possible to apply the same process to other middle distillate feeds with a lower or higher sulfur content. Other process modifications may be suitably used to treat other middle distillate feeds, and this is within the scope of the present invention, and preferably within the scope of the total oxidation, extraction, and distillation set out herein.

In the case of hydrotreated middle distillates, the invention process is technically and economically superior than conventional processes. The overall sulfur content is typically below 500 ppm_w. Hydrotreated middle distillates typically lack the lower molecular weight thiophenic compounds and are rich in higher molecular weight highly substituted dibenzothiophenes. As mentioned previously, these higher molecular weight highly substituted dibenzothiophenes are easier to oxidize. For this reason, as well as the lower total sulfur content of the feed, an overall decrease in the consumption of oxidant is expected. In addition, it may be possible to achieve total oxidation with a simpler oxidation system. Once oxidized, these higher molecular weight highly substituted dibenzothiophenes will have very high boiling points. Therefore, the ease of hydrocarbon recovery should increase, thereby allowing an improvement in the overall process yield. Potential yields of greater than 98 percent may be possible.

Appendix A	LAGO Distillation Curve
Appendix B	Component List
Appendix C1	Process Flow Diagrams
Appendix C2	Material Balances
Appendix D	Equipment List
Appendix E	Equipment Arrangements
Appendix F	Equipment Summary
Appendix G	Improved Oxidation Scheme

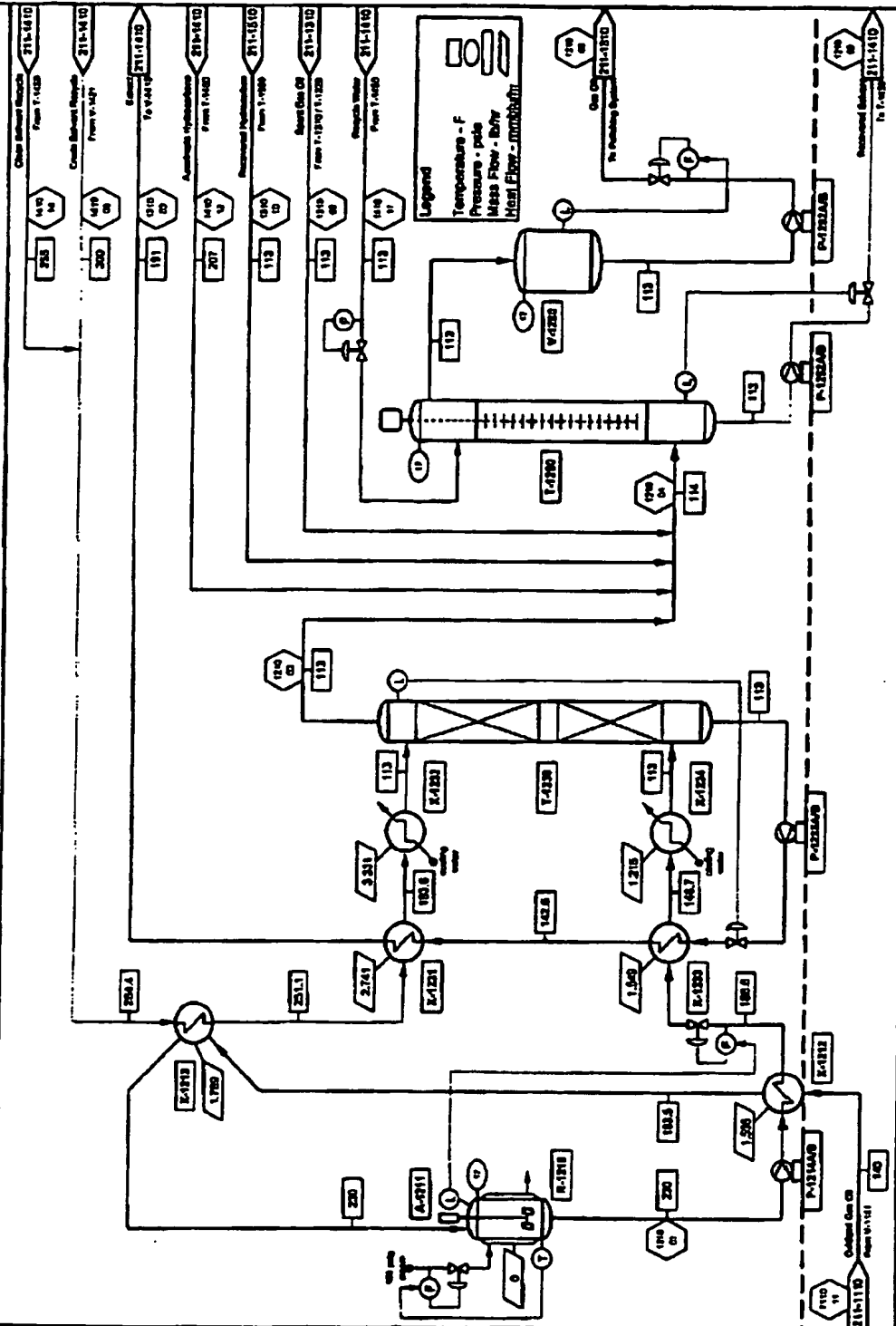
APPENDIX A - LAGO DISTILLATION CURVE



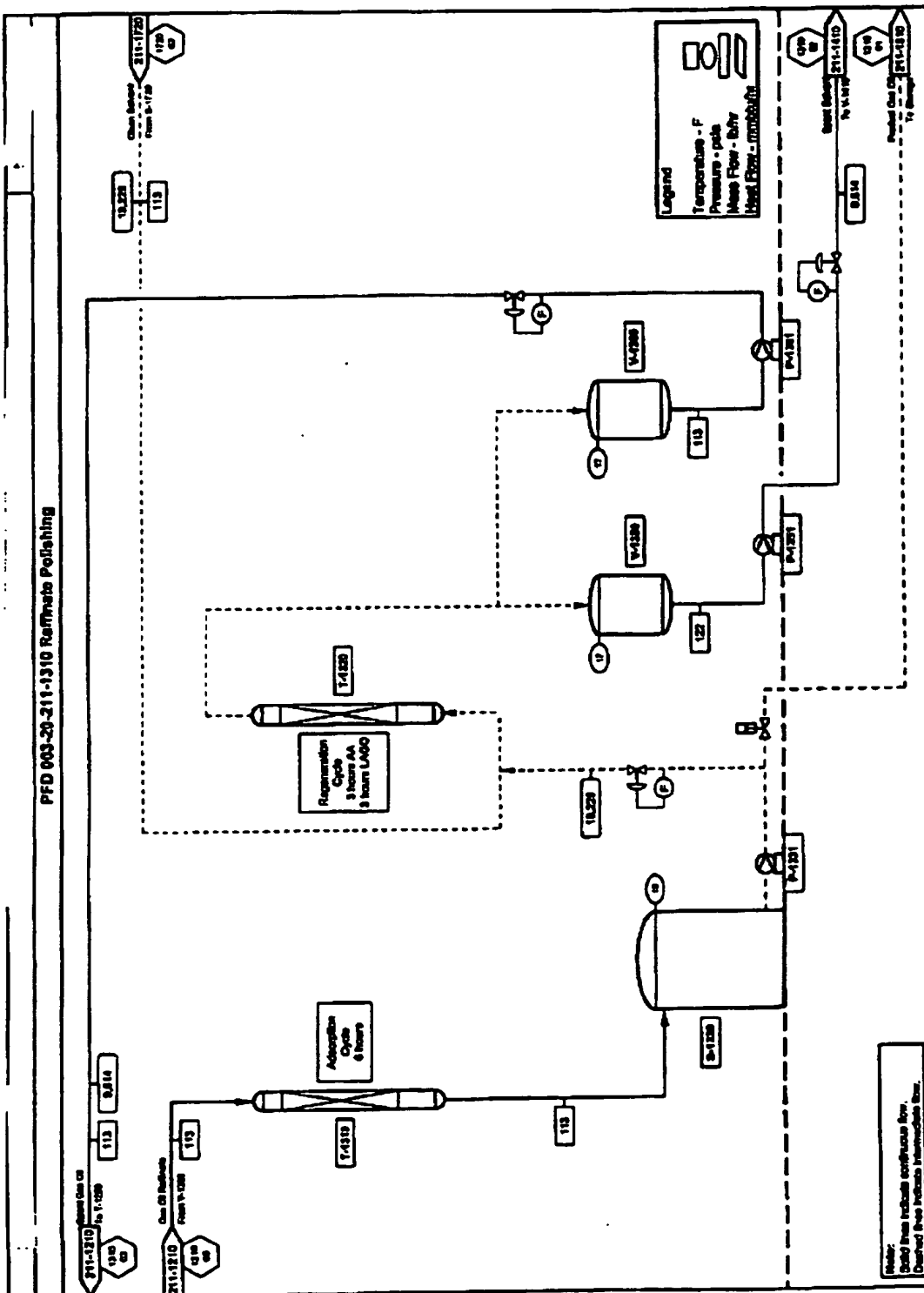
APPENDIX B - COMPONENT LIST

Boiling Fraction °F	Aliphatic Components	Aromatic Components	Thiophenic Components	Thiophenic Boiling Point °F	Sulphone Boiling P Int °F
< 156	n-Hexane				
156 - 209	2,2-Dimethylpentane	Benzene			
209 - 258	cis-1,2-Dimethylcyclopentane	Toluene			
258 - 303	2,4,4-Trimethylhexane	Ethylbenzene			
303 - 345	3,3,5-Trimethylheptane	Isopropylbenzene			
345 - 385	n-Butylcyclohexane	o-Diethylbenzene			
385 - 421	n-Undecane	1,2,3,4-Tetramethylbenzene			
421 - 456	n-Dodecane	Naphthalene	Benzothiophene	427.8	728.9
456 - 488	n-Tridecane	2-Methylnaphthalene	Methylbenzothiophene	482.8	777.6
488 - 519	n-Tetradecane	2,7-Dimethylnaphthalene	Ethylbenzothiophene	528.8	827.9
519 - 548	n-Pentadecane	1,2-Diphenylethane	m-Dimethylbenzothiophene	534.1	833.2
548 - 576	n-Hexadecane	Fluorene	1-Methyl-3-ethylbenzothiophene	574.0	873.2
576 - 602	n-Heptadecane	1-n-Pentylnaphthalene	1,2,3-Trimethylbenzothiophene	600.7	899.8
602 - 626	n-Octadecane	1-n-Hexylnaphthalene	Dibenzothiophene	628.6	927.8
626 - 651	n-Nonadecane	Anthracene	Dibenzothiophene	628.6	927.8
651 - 674	n-Eicosane	1,1,2-Triphenylethane	Naphthothiophene	676.0	975.2
674 - 695	n-Heneicosane	1,1,2,2-Tetraphenylethane	Methyldibenzothiophene	683.6	982.7
695 - 716	n-Doocosane	m-Terphenyl	2-Methylnaphthothiophene	717.7	1017
> 716	n-Tricosane	Pyrene	Ethylidibenzothiophene	729.6	1029

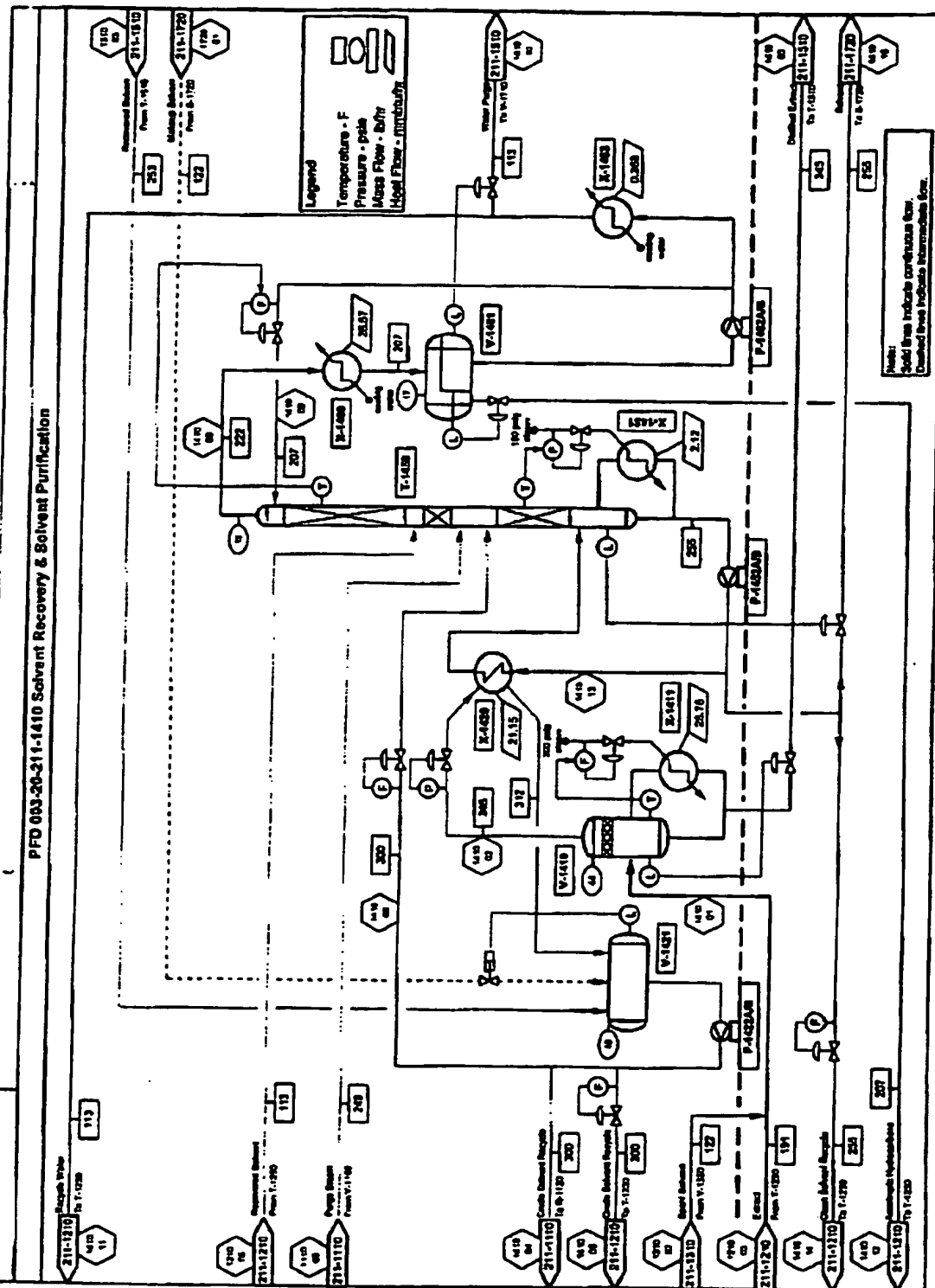
PFD 003-20-211-1210 Sulfox Extraction & Refillate Washing



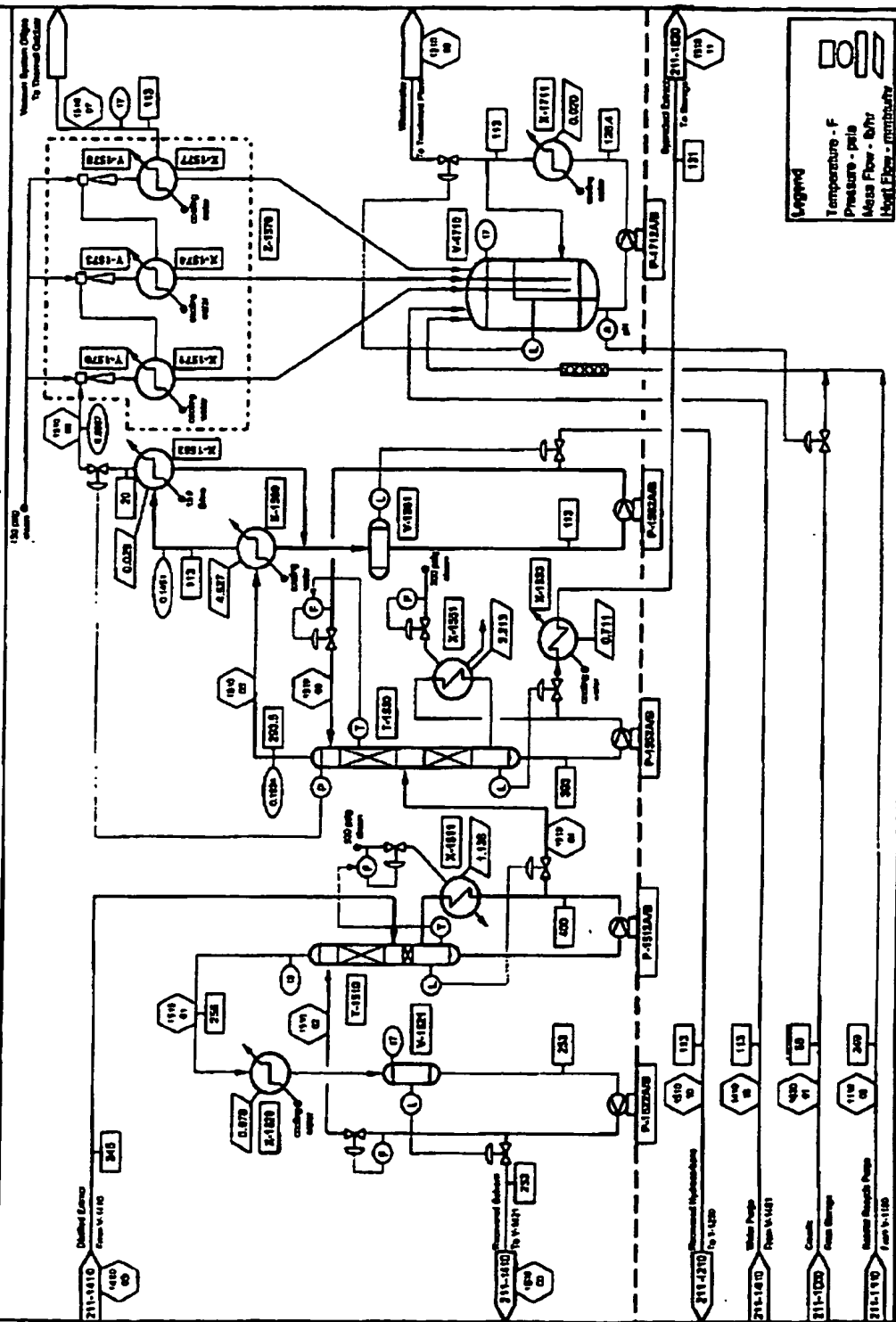
PFD 003-20-311-310 Refractive Polishing



PFD 003-20-211-1410 Solvent Recovery & Solvent Purification



PFD 003-20-211-1510 Hydrocarbon Recovery



APPENDIX C2 - MATERIAL BALANCES

Stream Number		101001	102001	103001	104001	111001	111002	111003	111004
Stream Description		Gas Oil Feed	Catalyst Makeup	25 wt% Caustic to Neutralization	Hydrogen Peroxide Feed	First Stage Oxidizer Feed	First Stage Oxidizer Effluent	First Stage Organic Phase	First Stage Aqueous Phase
Temperature	F	68.0	68.0	68.0	77.0	176.0	181.4	181.4	181.2
Pressure	psia	29.39	29.39	14.70	29.39	14.70	17.00	17.00	17.00
Total Flow	lbmol/hr	333.40	0.01	6.01	59.18	933.94	939.39	582.99	351.35
Total Flow	lb/hr	62842.3	0.9	125.5	1457.3	96819.7	96619.7	76941.4	19518.3
Total Flow	gpm	149.5	0.0	0.2	2.3	218.8	553.3	178.9	38.5
Total Flow	bbbl	5125.8	0.0	6.8	77.9	7500.1	18971.4	6167.2	1319.2
Mass Flow	lb/hr								
O ₂		0.0	0.0	0.0	0.0	0.0	160.0	0.0	0.0
N ₂		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H ₂ O		0.0	0.0	84.1	437.2	772.0	1287.9	138.6	1158.4
H ₂ O ₂		0.0	0.0	0.0	1020.1	993.0	0.0	0.0	0.0
H ₂ SO ₄		0.0	0.0	0.0	0.0	158.0	0.0	0.0	158.0
Acetic Acid		0.0	0.0	0.0	0.0	26754.5	26754.5	12750.3	14004.2
Aliphatics		41733.7	0.0	0.0	0.0	42381.8	42381.8	42070.3	311.5
Aromatics		19282.8	0.0	0.0	0.0	21469.5	21469.5	19625.1	1844.4
Thiophenes		1818.1	0.0	0.0	0.0	1818.1	72.6	58.7	14.0
Sulfones		0.0	0.0	0.0	0.0	2276.7	4327.2	2287.4	2029.8
Sodium Hydroxide		0.0	0.0	31.4	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Acetate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fraction	lb/lb								
O ₂		0.0000	0.0000	0.0000	0.0000	0.0000	0.0017	0.0000	0.0000
N ₂		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H ₂ O		0.0000	0.0200	0.7500	0.3000	0.0080	0.0134	0.0018	0.0593
H ₂ O ₂		0.0000	0.0000	0.0100	0.7000	0.0103	0.0000	0.0000	0.0000
H ₂ SO ₄		0.0000	0.0000	0.0000	0.0000	0.0016	0.0016	0.0000	0.0080
Acetic Acid		0.0000	0.0000	0.2500	0.0000	0.2769	0.2769	0.1657	0.7175
Aliphatics		0.6641	0.0000	0.0000	0.0000	0.4386	0.4386	0.5468	0.0160
Aromatics		0.3070	0.0000	0.0000	0.0000	0.2722	0.2272	0.2851	0.0945
Thiophenes		0.0289	0.0000	0.0000	0.0000	0.0198	0.0008	0.0008	0.0007
Sulfones		0.0000	0.0000	0.0000	0.0000	0.0236	0.0448	0.0286	0.1040
Sodium Hydroxide		0.0000	0.0000	0.2500	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Acetate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfur Content	ppm								
Actual		5099.3	32039.5	0.0	0.0	7397.9	7397.9	4818.0	19424.9
Feed Basis		5099.3	na	na	na	10520.2	10472.8	5545.0	85630.8
Physical Properties									
Density (liquid)	lb/gal	7.00	14.39	10.59	10.87	7.36	7.39	7.12	8.45
Density (vapor)	lb/lb	na	na	na	na	na	na	na	na
Heat Capacity	btu/lb-R	0.487	0.217	0.820	0.666	0.527	0.597	0.516	0.595
Viscosity	cP	3.639	20.519	na	1.032	na	na	0.867	0.644
Viscosity (light phase)	cP	na	na	na	na	0.827	na	na	na
Viscosity (heavy phase)	cP	na	na	na	na	0.559	na	na	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number	111005	111006	111007	111008	111009	111010	111011	111012
Stream Description	Flash Drum Vapor	Recycle Acid to First Stage	Recycle Acid to Second Stage	Reactor Recycle Purge	Second Stage Oxidizer Feed	Second Stage Oxidizer Effluent	Second Stage Organic Phase	Second Stage Aqueous Phase
Temperature	249.3	249.1	248.1	249.3	139.6	140.0	140.0	140.0
Pressure	18.00	18.00	18.00	18.00	17.00	17.00	17.00	17.00
Total Flow	247.86	0.00	102.88	0.52	744.65	744.65	514.53	230.12
Total Flow	11350.9	0.0	8127.8	40.8	88526.5	84538.5	73545.4	12881.1
Total Flow	8892.6	0.0	15.4	0.1	196.0	196.0	170.4	24.3
Total Flow	304890.4	0.0	528.0	2.7	6719.5	6719.9	5843.9	534.2
Mass Flow								
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O	1050.3	0.0	107.8	0.5	684.3	688.7	58.2	640.4
H2O2	0.0	0.0	0.0	0.0	1020.1	993.0	0.0	983.0
H2SO4	0.1	0.0	156.0	0.8	156.0	156.0	0.0	156.0
Acetic Acid	10003.9	0.0	3880.3	20.0	16730.8	16730.8	9205.7	7824.9
Aliphatics	69.6	0.0	240.7	1.2	42311.0	42311.0	42179.1	131.9
Aromatics	228.5	0.0	1609.8	8.1	21234.9	21234.9	18976.7	1258.3
Thiophenes	0.2	0.0	13.7	0.1	72.4	0.0	0.0	0.0
Sulfones	0.0	0.0	2019.6	10.1	4317.1	4402.2	2125.6	2276.8
Sodium Hydroxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Acetate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fraction								
O2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O	0.0025	0.0132	0.0132	0.0132	0.0079	0.0081	0.0098	0.0493
H2O2	0.0000	0.0000	0.0000	0.0000	0.0118	0.0115	0.0000	0.0765
H2SO4	0.0000	0.0192	0.0182	0.0181	0.0018	0.0018	0.0000	0.0120
Acetic Acid	0.8814	0.4897	0.4887	0.4898	0.1934	0.1834	0.1252	0.5797
Aliphatics	0.0081	0.0286	0.0296	0.0286	0.4890	0.4890	0.5735	0.0102
Aromatics	0.0020	0.1881	0.1881	0.1881	0.2434	0.2454	0.2716	0.0869
Thiophenes	0.0000	0.0017	0.0017	0.0017	0.0008	0.0000	0.0000	0.0000
Sulfones	0.0000	0.2485	0.2485	0.2485	0.0488	0.0509	0.0288	0.1764
Sodium Hydroxide	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfate	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Acetate	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfur Content	ppmw							
Actual	5.0	44052.1	44052.1	44022.5	6242.7	6242.7	4335.9	30378.5
Fuel Basis	180.0	44052.1	82167.5	82115.6	10488.4	10488.4	4980.8	107539.3
Physical Properties								
Density (liquid)	lb/gal	8.79	8.79	8.79	7.35	7.35	7.19	8.68
Density (vapor)	lb/ft3	na	na	na	na	na	na	na
Heat Capacity	btu/lb-R	0.159	0.572	0.572	0.486	0.488	0.483	0.487
Viscosity	cp	0.012	0.497	0.497	na	na	1.278	0.745
Viscosity (light phase)	cp	na	na	na	1.235	1.235	na	na
Viscosity (heavy phase)	cp	na	na	na	0.765	0.762	na	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number		121001	121002	121003	121004	121005	121006	131001	131002
Stream Description		Distillate Reactor Effluent	Sulfur Extraction Raffinate	Sulfur Extraction Extract	Wash Column Feed	Wash Column Extract	Gas Oil to Refining	Product Gas Oil to Storage	Spent Acetic Acid
Temperature									
Pressure		230.0	113.0	113.0	110.4	113.0	113.0	113.0	110.7
Total Flow	lb-mol/hr	914.53	28.38	1840.21	523.27	384.85	353.49	14.70	73.48
Total Flow	lb/hr	73545.4	46284.6	19179.4	75270.0	12888.8	65437.8	270.32	152.33
Total Flow	gpm	178.7	112.0	228.7	178.0	23.8	184.1	138.4	10023.3
Total Flow	bbbl	6128.4	3839.3	7875.5	8035.4	885.4	5824.7	4779.9	20.2
Mass Flow	lb/hr								691.5
O2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O		58.2	1.7	604.4	16.5	3701.1	16.5	0.0	53.2
H2O2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2SO4		0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Acetic Acid		8205.7	8315.6	88301.8	8159.8	8834.5	388.7	0.0	7459.9
Aliphatics		42179.1	35598.5	8338.0	46985.8	2.3	48984.8	40143.7	1742.8
Aromatics		19978.7	4373.0	18116.1	19101.8	89.2	19043.8	18270.9	762.8
Triphenyls		0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Sulfones		2125.6	5.8	2121.2	5.9	1.7	4.2	0.0	4.7
Sodium Hydroxide		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Acetate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fraction	lb/lb								
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0088	0.0000	0.0051	0.0002	0.2840	0.0002	0.0000	0.0043
H2O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Acetic Acid		0.1252	0.1384	0.7483	0.1217	0.7010	0.0558	0.0000	0.7443
Aliphatics		0.5735	0.7890	0.0699	0.6342	0.0002	0.7072	0.7116	0.1739
Aromatics		0.2716	0.0945	0.1579	0.2538	0.0047	0.2856	0.2884	0.0781
Triphenyls		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfones		0.0288	0.0001	0.0178	0.0001	0.0001	0.0001	0.0000	0.0006
Sodium Hydroxide		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Acetate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfur Content	ppmw								
Actual		4335.9	18.9	2870.5	12.2	21.2	9.8	0.0	71.2
Fuel Basis		4860.8	21.9	10872.3	13.9	4220.0	9.9	0.0	284.3
Physical Properties									
Density (liquid)	lb/pt	6.85	6.86	6.84	7.12	8.12	8.74	6.74	8.28
Density (vapor)	lb/ft3	na	na	na	na	na	na	na	na
Heat Capacity	Btu/lb-R	0.536	0.491	0.435	0.473	0.687	0.470	0.470	0.454
Viscosity	cP	0.877	1.447	0.922	1.565	0.701	1.881	1.881	0.923
Viscosity (light phase)	cP	na	na	na	na	na	na	na	na
Viscosity (heavy phase)	cP	na	na	na	na	na	na	na	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number	Stream Description	131003 Spent Gas Oil	141001 Feed to Solvent Recovery Flash	141002 Vapor from Solvent Recovery Flash	141003 Liquid from Solvent Recovery Flash	141004 Recovered Acid to First Stage	141005 Recovered Acid to Sulfur Extractor	141006 Recovered Acid to Purification	141008 Oxid Vapor from Purification Column
Temperature	F	103.7	185.3	342.9	342.9	299.9	299.9	288.9	222.3
Pressure	psia	73.48	44.09	44.09	44.09	44.09	44.09	44.09	18.00
Total Flow	lb-mol/hr	82.47	1892.54	1771.74	220.80	389.41	1181.35	285.34	1468.03
Total Flow	lb/hr	9813.8	129202.7	100021.1	29181.5	20768.0	65684.0	16871.0	25355.8
Total Flow	gpm	21.6	282.4	28118.3	68.5	48.7	149.8	37.5	67112.5
Total Flow	baud	739.0	8998.4	998340.1	2281.3	1601.8	5138.1	1284.0	2300988.8
Mass Flow	lb/hr								
O2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O		12.0	557.5	550.0	7.6	131.5	421.8	105.4	29984.8
H2SO4		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetic Acid		2393.1	98781.5	97403.0	4358.5	19228.7	61681.7	18415.4	347.8
Aliphatics		5176.5	19078.8	2508.6	7570.0	516.2	1855.3	413.8	354.4
Aromatics		2073.0	18578.9	4459.3	15119.6	818.5	2845.2	756.3	636.8
Thiophenes		0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.1
Sulfones		0.1	2138.0	0.2	2125.7	0.0	0.1	0.0	0.0
Sodium Hydroxide		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Acetate		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fraction	wt%								
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0013	0.0051	0.0063	0.0003	0.0063	0.0063	0.0063	0.0063
H2SO4		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Acetic Acid		0.2448	0.7488	0.9238	0.1494	0.9247	0.9247	0.9247	0.9247
Aliphatics		0.5383	0.0780	0.0251	0.2594	0.0248	0.0248	0.0248	0.0140
Aromatics		0.2156	0.1515	0.0448	0.5181	0.0442	0.0442	0.0442	0.0260
Thiophenes		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfones		0.0000	0.0165	0.0000	0.0728	0.0000	0.0000	0.0000	0.0000
Sodium Hydroxide		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Acetate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfur Content	ppm								
Actual		2.1	2488.8	0.4	10229.6	0.4	0.4	0.4	0.0
Fuel Basis		2.8	10038.1	5.4	12852.7	5.2	5.2	5.2	0.0
Physical Properties									
Density (liquid)	lb/mol	7.43	8.20	na	7.30	7.41	7.41	7.41	na
Density (vapor)	lb/lb	na	na	0.428	na	na	na	na	0.647
Heat Capacity	btu/lb-R	0.477	0.481	1.050	0.541	0.653	0.653	0.653	0.572
Viscosity (light phase)	cP	1.353	0.567	0.013	0.435	0.299	0.298	0.298	0.013
Viscosity (heavy phase)	cP	na	na	na	na	na	na	na	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number	141009	141010	141011	141012	141013	141014	141015	151001
Stream Description	Reflux to Purification Column	Water Purge from Purification Column	Solvent Water to Wash Column	Distillate from Purification	Acetic Acid to Reboiler	Purified Acid to Sulfon Extractor	Purified Acid to Storage	Vapor Distillate Acid Res Column
Temperature								
Pressure	208.8	113.0	18.00	206.8	255.1	255.1	255.1	255.8
Flow								
lb-mol/hr	1174.42	59.51	225.07	9.02	6371.22	489.54	176.00	108.88
Total Flow	19603.8	99.3	3798.9	1001.7	35000.0	25344.6	8613.8	6122.4
lb/hr	42.8	2.0	7.7	2.6	745.9	53.8	20.5	3447.4
Total Flow	1460.4	69.9	264.3	80.3	25372.8	1844.5	704.0	118188.0
Mass Flow								
lb/hr								
O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O	19312.1	978.6	3701.1	2.8	1748.9	128.2	48.1	11.4
H2O2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2SO4	0.0	0.0	0.0	0.0	0.9	0.1	0.0	0.0
Acetic Acid	279.1	14.1	53.5	1.1	343136.3	24749.8	9425.3	5784.8
Aliphatics	6.8	0.3	1.3	345.9	1367.7	100.1	38.1	115.1
Aromatics	5.8	0.3	1.1	651.8	3703.3	287.1	101.7	211.2
Thiophenes	0.0	0.0	0.0	0.1	1.0	0.1	0.0	0.0
Sulfones	0.0	0.0	0.0	0.0	17.8	1.3	0.8	0.0
Sodium Hydroxide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Sulfide	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Acetate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fraction								
O2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
N2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O	0.9851	0.9851	0.9851	0.0028	0.0050	0.0050	0.0050	0.0019
H2O2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Acetic Acid	0.0142	0.0142	0.0142	0.0011	0.9804	0.9804	0.0040	0.9448
Aliphatics	0.0003	0.0003	0.0003	0.3463	0.0040	0.0040	0.0040	0.0183
Aromatics	0.0003	0.0003	0.0003	0.8507	0.0106	0.0106	0.0106	0.0345
Thiophenes	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000
Sulfones	0.0000	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001	0.0000
Sodium Hydroxide	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfide	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Acetate	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfur Content	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Actual	0.0	0.0	0.0	10.5	9.1	9.1	9.1	0.0
Fuel Basis	5.8	5.8	5.8	10.5	628.2	628.2	628.2	0.0
Physical Properties								
Density (liquid)	7.87	8.12	8.12	6.33	7.81	7.81	7.80	na
Density (vapor)	na	na	na	na	na	na	na	0.221
Heat Capacity	0.987	0.928	0.928	0.520	0.555	0.555	0.559	0.959
Viscosity	0.289	0.812	0.812	0.381	0.372	0.372	0.367	0.012
Viscosity (light phase)	na	na	na	na	na	na	na	na
Viscosity (heavy phase)	na	na	na	na	na	na	na	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number		151002	151003	151004	151005	151006	151007	151008	151009
Stream Description		Refux to Add Rec Column	Rec Acid from Add Rec Column	Bottoms from Add Rec Column	Overhd Vapor from Hyd Rec Column	Vapor to Vacuum System	Offgas to Thermal Oxidizer	Wastewater to Treatment Plant	Refux to Hyd Rec Column
Temperature	F	253.1	253.1	356.5	294.1	20.0	113.0	115.5	112.4
Pressure	psia	18.00	18.00	18.00	0.19	0.19	17.40	17.40	0.18
Total Flow	lb-mol/hr	38.23	72.45	148.35	134.78	0.73	0.50	88.20	17.48
Total Flow	lb/hr	2040.8	4081.6	25098.9	21140.8	27.7	14.2	1487.8	2783.1
Total Flow	gpm	4.4	8.8	60.6	643009.1	1927.8	20.2	2.8	6.0
Total Flow	boepd	150.3	300.6	2078.7	22046021.1	66080.5	883.1	66.9	285.4
Mass Flow	lb/hr								
O2		0.0	0.0	0.0	3.0	3.0	2.6	0.0	0.0
N2		0.0	0.0	0.0	10.0	9.9	9.1	0.0	0.0
H2O		3.6	7.6	0.0	0.0	0.0	0.7	1402.6	0.0
H2O2		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2SO4		0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Acetic Acid		1928.3	3856.5	502.0	575.6	12.0	0.0	0.0	0.0
Aliphatics		38.4	76.7	7493.3	6746.8	1.3	0.9	2.0	73.5
Aromatics		70.4	140.8	14878.8	13805.5	1.4	0.9	8.9	878.8
Thiophenes		0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0
Sulfones		0.0	0.0	2125.7	0.0	0.0	0.0	10.1	0.0
Sodium Hydroxide		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Sulfate		0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0
Sodium Acetate		0.0	0.0	0.0	0.0	0.0	0.0	63.0	0.0
Mass Fraction	lb/lb								
O2		0.0000	0.0000	0.0000	0.0001	0.1094	0.1817	0.0000	0.0000
N2		0.0000	0.0000	0.0000	0.0005	0.3588	0.8437	0.0000	0.0000
H2O		0.0018	0.0019	0.0000	0.0000	0.0000	0.0466	0.8427	0.0000
H2O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2SO4		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Acetic Acid		0.9448	0.9448	0.0000	0.0272	0.4338	0.0008	0.0000	0.0267
Aliphatics		0.0188	0.0188	0.2985	0.3181	0.0484	0.0638	0.0013	0.3186
Aromatics		0.0345	0.0345	0.5968	0.6530	0.0507	0.0945	0.0080	0.6538
Thiophenes		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sulfones		0.0000	0.0000	0.0847	0.0000	0.0000	0.0000	0.0068	0.0000
Sodium Hydroxide		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Sodium Sulfate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0000
Sodium Acetate		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0423	0.0000
Sulfur Content	ppmw								
Actual		0.0	0.0	12706.9	0.7	0.0	0.0	1208.4	0.7
Fuel Basis		0.0	0.0	12888.3	0.7	0.0	0.0	85330.7	0.7
Physical Properties									
Density (liquid)	lb/gal	7.84	7.75	6.89	na	na	na	8.11	7.68
Density (vapor)	lb/ft3	na	na	na	0.00410	0.00179	0.087	na	na
Heat Capacity	Btu/lb-R	0.512	0.524	0.550	0.428	0.427	0.288	0.822	0.417
Viscosity	cP	0.390	0.369	0.456	0.007	0.013	0.016	na	2.177
Viscosity (light phase)	cP	na	na	na	na	na	na	0.569	na
Viscosity (heavy phase)	cP	na	na	na	na	na	na	2.708	na

APPENDIX C2 - MATERIAL BALANCES

Stream Number		151010	151011
Stream Description		Hyd Rec	Byproduct Entry to Storage
Temperature	F	112.4	131.0
Pressure	psia	0.19	17.00
Total Flow	lb-mol/hr	116.96	31.34
Total Flow	lb/hr	16350.0	6725.3
Total Flow	gpm	39.9	12.6
Total Flow	bpsd	1369.5	439.3
Mass Flow	lb/hr		
O2		0.0	0.0
N2		0.1	0.0
H2O		0.0	0.0
H2O2		0.0	0.0
H2SO4		0.0	0.1
Acetic Acid		480.0	0.0
Aliphatics		5665.5	1628.1
Aromatics		12004.0	2873.3
Thiophenes		0.0	0.0
Sulfones		0.0	2125.7
Sodium Hydroxide		0.0	0.0
Sodium Sulfate		0.0	0.0
Sodium Acetate		0.0	0.0
Mass Fraction	lb/lb		
O2		0.0000	0.0000
N2		0.0000	0.0000
H2O		0.0000	0.0000
H2O2		0.0000	0.0000
H2SO4		0.0000	0.0000
Acetic Acid		0.0267	0.0000
Aliphatics		0.3185	0.2418
Aromatics		0.6539	0.4421
Thiophenes		0.0000	0.0000
Sulfones		0.0000	0.3181
Sodium Hydroxide		0.0000	0.0000
Sodium Sulfate		0.0000	0.0000
Sodium Acetate		0.0000	0.0000
Sulfur Content	ppmw		
Actual		0.7	47422.9
Fuel Basis		0.7	47423.4
Physical Properties			
Density (liquid)	lb/gal	7.86	8.75
Density (vapor)	lb/ft3	na	na
Heat Capacity	lb/lb-R	0.417	0.343
Viscosity	cP	2.177	8.683
Viscosity (light phase)	cP	na	na
Viscosity (heavy phase)	cP	na	na

Process Columns, Vessels, Tanks																
Item Number	Description	PFD	Q	Unit	Diastol. Incl.	T-T Incl.	Motor hp	MOC	Internals	DP PSIG	OT F	Consumption lbs/hr	Reaction Volume BBL/HR	Total Volume BBL/HR	Orientation	Remarks
R-1110	1st Stage Oxidizer	211-1120	1	Turn Column	5.0	38	50	Alloy 20	Perforated Plates & Alloy 20 Baffles	50.8 PV	682	18.6	4992	5381	Vertical	Mounted on 29 CS Bldg. Over Head. Top Head & Flat Bottom Head = ASME FAD
T-1290	Raffinate Wash Column	211-1210	1	Spherical Column	5.0	40	20	316 SS	3" 316 SS Agitated Stack	50.8 PV	682	7.5	NA	9049	Vertical	Mounted on 29 CS Bldg. Double Mechanical Drive Top Head & Flat Bottom Head = ASME FAD
R-1210	Distilled Reactor	211-1210	1	Assembled Vessel	0.5	6.0	ASME FAD	316 SS	2" 316 SS Baffles 50 Degrees Apart	50.8 PV	682	1800	2151	2310	Vertical	316 SS Corrosion Resistant. Mounted on DP = 500 psig & PV; Mounted on Legs
S-1040	Hydrogen Peroxide Storage Tank	211-1040	1	API Storage Tank	18	16	Dome / Flat	316 SS	NA	2.5 g - 0.14	300	20,000	24,084	28,538	Vertical	Provides fire under deluge system on outside of tank and process water. Mounted on Concrete Pad
T-1230	Sulfur Extraction Column	211-1210	1	Packed Column	7.5	54	ASME FAD	316 SS	2" 316 SS SAMP Packed Bed	50.8 PV	682	NA	NA	15349	Vertical	Mounted on 29 CS Bldg
T-1310	Raffinate Polishing Column	211-1310	1	Adsorption Column	5.0	42	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	8318	Vertical	Size based on a total cycle of 12 hours (8 online, 0 regenerating). Mounted on 29 CS Bldg
T-1280	Raffinate Polishing Column	211-1210	1	Adsorption Column	5.0	42	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	8318	Vertical	Size based on a total cycle of 12 hours (8 online, 0 regenerating). Mounted on 29 CS Bldg
T-1650	Solvent Purification Column	211-1610	1	Packed Column	7.0	87	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	24012	Vertical	Size based on a total cycle of 12 hours (8 online, 0 regenerating). Mounted on 29 CS Bldg
T-1510	Solvent Recovery Column	211-1510	1	Packed Column	1.5	25	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	334	Vertical	Size based on a total cycle of 12 hours (8 online, 0 regenerating). Mounted on 29 CS Bldg
T-1520	Solvent Recovery Column	211-1510	1	Packed Column	7.0	28	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	8473	Vertical	Size based on a total cycle of 12 hours (8 online, 0 regenerating). Mounted on 29 CS Bldg
V-1120	1st Stage Distillate Oil Separator	211-1120	1	UL Separator	8.00	19.50	ASME FAD	Alloy 20	Overbur Baffle	50.8 PV	682	NA	NA	8684	Horizontal	Mounted on Saddle
V-1141	Distillate Separator	211-1120	1	UL Separator	9.00	10.50	ASME FAD	Alloy 20	Overbur Baffle	50.8 PV	682	NA	NA	8684	Horizontal	Mounted on Saddle
V-1461	Solvent Purification Column	211-1410	1	UL Separator	3.50	6.50	ASME FAD	316 SS	Overbur Baffle	50.8 PV	682	NA	NA	520	Horizontal	Mounted on Saddle
V-1290	Raffinate Hold Vessel	211-1210	1	Surge Drum	7.0	12.0	ASME FAD	316 SS	NA	50.8 PV	682	2000	3081	3089	Vertical	Mounted on Legs
S-1300	Product Hold Tank	211-1310	1	2M Storage Tank	20	18	Dome / Flat	CS	NA	2.5 g - 0.14	810	26,000	42,383	47,190	Vertical	Mounted on Concrete Pad
V-1250	Spent Acetic Acid Hold Vessel	211-1310	1	Surge Drum	8.0	18.0	ASME FAD	316 SS	NA	50.8 PV	682	3800	8124	8634	Vertical	Mounted on Legs
V-1300	Spent Oil Hold Vessel	211-1310	1	Surge Drum	8.0	18.0	ASME FAD	316 SS	NA	50.8 PV	682	4800	8124	8634	Vertical	Mounted on Legs
V-1400	Wetted Flash Vessel	211-1410	1	VL Separator	4.0	10.0	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	1017	Vertical	Mounted on Legs
V-1410	Solvent Flash Vessel	211-1410	1	VL Separator	7.0	15.0	ASME FAD	316 SS	2" 15 Beds Raffinate City	50.8 PV	682	NA	NA	4722	Vertical	Mounted on 29 CS Bldg
V-1421	Solvent Flash Vessel	211-1410	1	Surge Drum	7.0	14.0	ASME FAD	316 SS	NA	50.8 PV	682	2100	3178	4444	Horizontal	Mounted on Saddle
V-1521	Solvent Recovery Column	211-1510	1	Surge Drum	2.5	4.0	ASME FAD	316 SS	Overbur Baffle	50.8 PV	682	NA	NA	2059	Vertical	Mounted on Legs
V-1501	Acetone Recovery Column	211-1510	1	Surge Drum	3.5	6.0	ASME FAD	304 SS	NA	50.8 PV	682	200	411	494	Horizontal	Mounted on Saddle
V-1710	Organic Vapor Separator	211-1720	1	Surge Drum	6.0	9.5	ASME FAD	Alloy 20	Overbur Baffle	50.8 PV	682	NA	NA	2059	Vertical	Mounted on Legs
S-1720	Solvent Hold Tank	211-1720	1	2M Storage Tank	10	16	Dome / Flat	316 SS	NA	2.5 g - 0.14	255	20,000	24,084	28,538	Vertical	Mounted on Concrete Pad
V-1140	Acetone Recovery Column	211-1710	1	VL Separator	6.0	8.0	ASME FAD	CS	NA	50.8 PV	682	NA	NA	1326	Vertical	Size was ultimately changed. Mounted on Legs
V-1710	Organic Vapor Separator	211-1710	1	VL Separator	6.0	8.0	ASME FAD	CS	NA	50.8 PV	682	NA	NA	1326	Vertical	Size was ultimately changed. Mounted on Legs
V-1760	Emergency Relief System Knockout Vessel	211-1760	1	VL Separator	7.0	14.0	ASME FAD	CS	NA	50.8 PV	682	NA	NA	4444	Horizontal	Size was ultimately changed. Mounted on Saddle

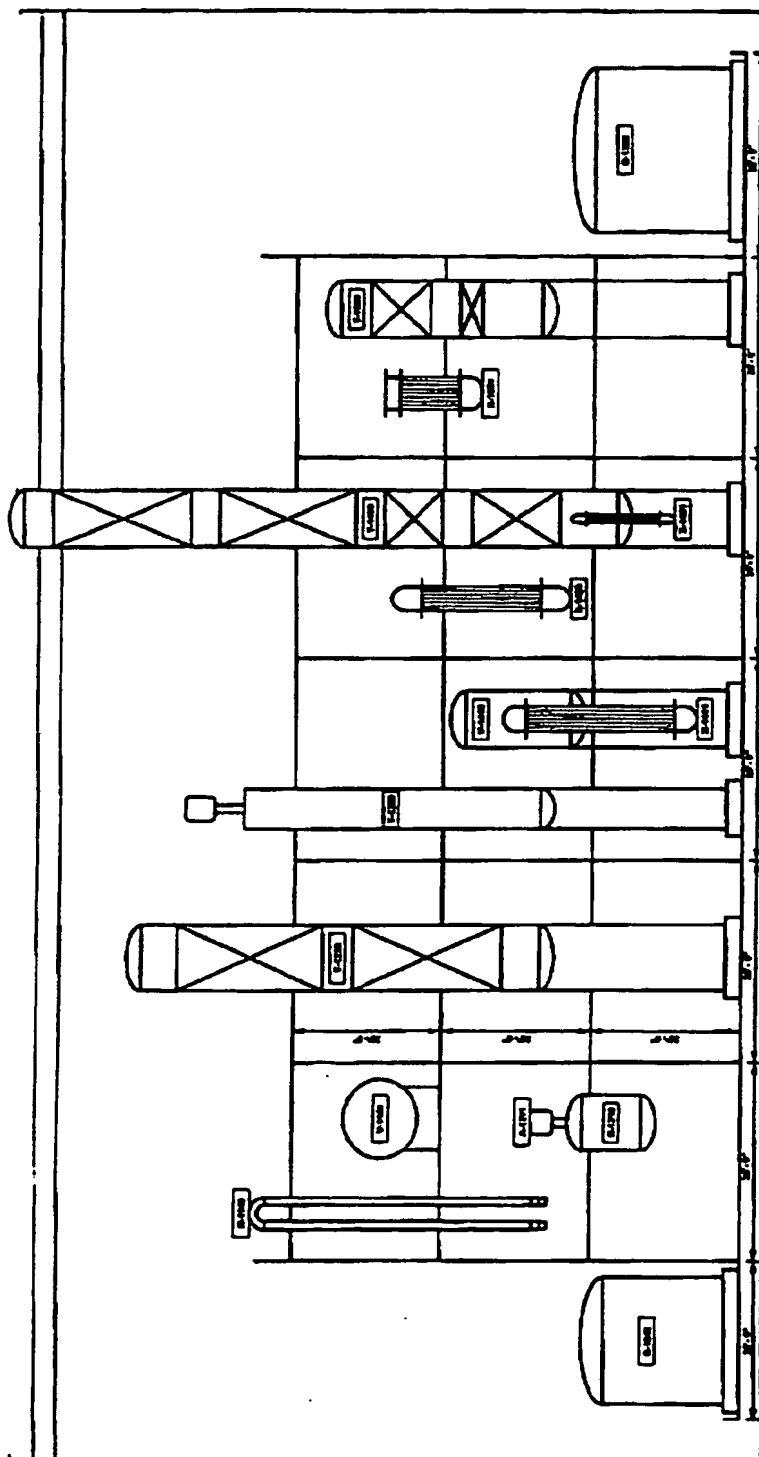
Heat Exchangers

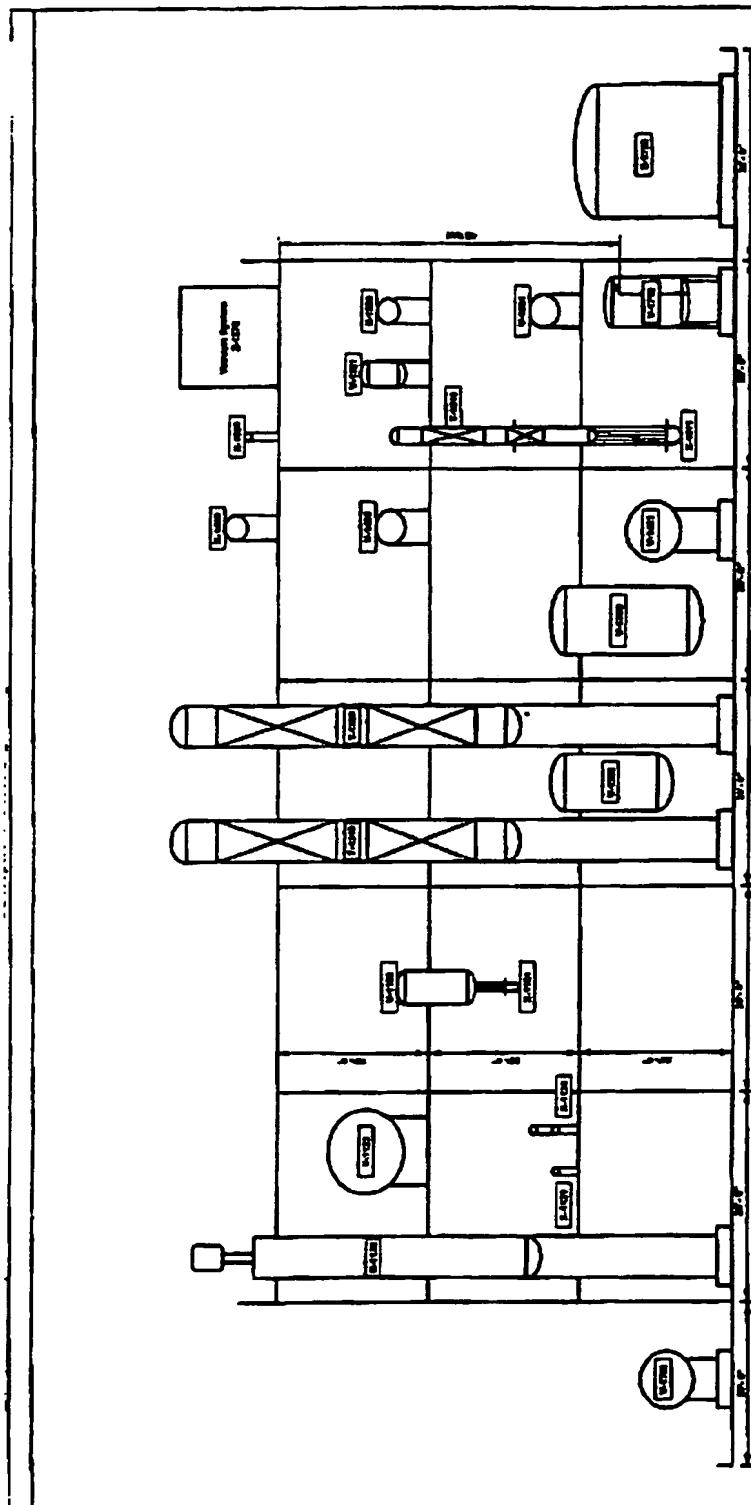
Item Number	Description	PFD #	22 Q	Type	Duty methanol	Area ft ²	Size 3 X T A L	Shell Tubes	MOC	Shell DP psig	OT F	Tubes DP psig	OT F	Orientation	Remarks
X-1121	Gas Oil Feed Heater	211-1110	1	Shell & Tube	0.50	124	8.625' / 16' / 16.8'	CS	CS	200.6	682	150.6	682	Horizontal	
X-1124	Discharge Interchange	211-1110	1	Shell & Tube	2.08	807	14' / 16' / 17.9'	CS	Alloy 20	150.6	682	150.6	682	Horizontal	Requires two shells in series
X-1161	Water Flash Vessel	211-1110	1	Shell & Tube	3.39	231	12.75' / 16' / 13.9'	CS	Monobloy C2/B	200.6	682	50.6 PV	682	Vertical	Thermosiphon Reboiler
X-1212	Electrical Reactor Feed Interchange	211-1210	1	Shell & Tube	1.60	544	16' / 16' / 17.9'	316 SS	316 SS	100.6	682	150.6	682	Horizontal	
X-1213	Desolved Reactor Feed Interchange	211-1210	1	Shell & Tube	1.79	319	10.75' / 20' / 22.1'	316 SS	316 SS	100.6	682	150.6	682	Horizontal	
X-1231	Column Solvent Interchange	211-1210	1	Shell & Tube	2.74	768	16' / 20' / 22.2'	316 SS	316 SS	150.6	682	150.6	682	Horizontal	
X-1232	Solvent Extraction Column Solvent Cycle Solvent Extraction	211-1210	1	Shell & Tube	3.33	709	16' / 18' / 20.6'	316 SS	316 SS	150.6	682	120.6	682	Horizontal	
X-1233	Column Feed / Effluent Interchange	211-1210	1	Shell & Tube	1.55	766	16' / 20' / 22.3'	316 SS	316 SS	150.6	682	150.6	682	Horizontal	
X-1234	Solvent Extraction Column Feed Cycle Solvent Flash Vessel	211-1210	1	Shell & Tube	1.22	420	12.75' / 16' / 19.6'	316 SS	316 SS	150.6	682	120.6	682	Horizontal	
X-1411	Solvent Flash Vessel	211-1410	1	Shell & Tube	28.76	2998	30' / 20' / 27'	CS	316 SS	350.6	682	50.6 PV	682	Vertical	Thermosiphon Reboiler
X-1420	Overhead Condenser	211-1410	1	Tube	21.15	2669	34' / 16' / 22.2'	316 SS	316 SS	50.6 PV	682	50.6 PV	682	Vertical	Primary Reboiler for T-1450; Forced Circulation on Tube
X-1451	Solvent Purification Column Trim Reboiler	211-1410	1	Shell & Tube	2.12	198	10.75' / 10' / 13.1'	CS	316 SS	200.6	682	50.6 PV	682	Vertical	Thermosiphon Reboiler
X-1460	Solvent Purification Column Overhead	211-1410	1	Shell & Tube	26.57	1077	34' / 16' / 11.1'	316 SS	316 SS	50.6 PV	682	120.6	682	Horizontal	Primary Reboiler for T-1450; Forced Circulation on Tube
X-1463	Solvent Purification Column Water Distillate	211-1410	1	Shell & Tube	0.37	60	6.625' / 12' / 13.4'	316 SS	316 SS	150.6	682	120.6	682	Horizontal	
X-1511	Solvent Recovery Column	211-1510	1	Shell & Tube	1.14	1005	16' / 20' / 22.7'	CS	316 SS	350.6	682	50.6 PV	682	Vertical	Forced Circulation on Tube
X-1520	Solvent Recovery Column Overhead	211-1510	1	Shell & Tube	0.86	49	10.75' / 4' / 6.7'	316 SS	316 SS	50.6 PV	682	120.6	682	Horizontal	
X-1531	Hydrocarbon Recovery Column Bottoms	211-1510	1	Shell & Tube	2.21	2425	42' / 8' / 13.0'	CS	7 CS 7	350.6	682	50.6 PV	682	Vertical	Falling Film Reboiler
X-1533	Hydrocarbon Recovery Column Bottoms	211-1510	1	Shell & Tube	0.71	124	10.75' / 16' / 17.7'	CS	7 CS 7	150.6	682	120.6	682	Horizontal	
X-1560	Hydrocarbon Recovery Column Overhead	211-1510	1	Shell & Tube	4.33	3666	40' / 14' / 17.7'	316 SS	316 SS	50.6 PV	682	120.6	682	Horizontal	Low pressure drop design requires vapor bell to minimize pressure drop at bundle entrance
X-1563	Hydrocarbon Recovery Column	211-1510	1	Shell & Tube	0.03	256	14' / 14' / 15.5'	316 SS	316 SS	50.6 PV	682	120.6	682	Horizontal	Low pressure drop design requires vapor bell to minimize pressure drop at bundle entrance
X-1711	Neutralization Vessel	211-1110	1	Shell & Tube	0.02	15	6.625' / 4' / 15.3'	Alloy 20	Alloy 20	50.6 PV	682	120.6	682	Horizontal	
X-1721	Solvent Hold Tank	211-1720	1	Shell & Tube	0.86	84	6.625' / 12' / 18.3'	316 SS	316 SS	50.6 PV	682	120.6	682	Horizontal	

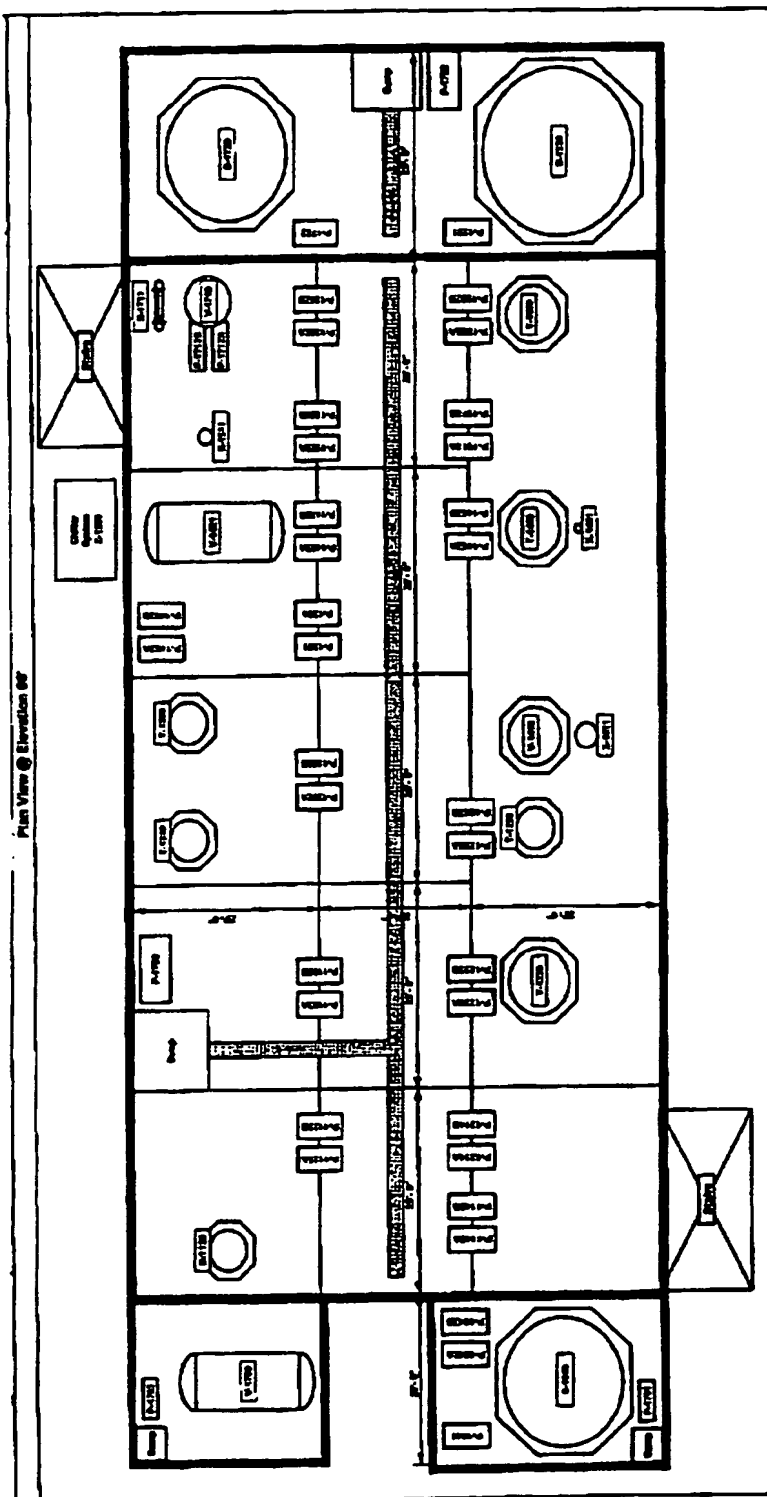
Pumps											Remarks
Item Number	Description	PFD	Q	Type	Capacity gpm	Head feet	Motor hp	MOC	Mechanical Seal	DP psi	
P-1041	Peroxide Unloading Pump	211-1040	1	Centrifugal	100	28	3.0	316 SS	Single Mechanical FV	150 &	Horizontal
P-1042A/B	Peroxide Feed Pump	211-1040	2	Centrifugal	15	125	7.5	316 SS	Single Mechanical FV	150 &	Horizontal
P-1123A/B	1st Stage Oxidizer Oil Pump	211-1110	2	Centrifugal	188	85	10.0	Alloy 20	Seal-less FV	150 &	Horizontal
P-1142A/B	Oxidant Recycle Pump	211-1110	2	Centrifugal	25	66	3.0	Alloy 20	Double Mechanical FV	150 &	Horizontal
P-1162A/B	Water Flush Vessel	211-1110	2	Centrifugal	18	82	5.0	Hastelloy C276	Double Mechanical FV	150 &	Horizontal
P-1214A/B	Desolvent Reactor	211-1210	2	Centrifugal	187	226	20.0	316 SS	Seal-less FV	150 &	Horizontal
P-1238A/B	Discharge Pump Sulfon Extraction	211-1210	2	Centrifugal	260	53	7.5	316 SS	Seal-less FV	150 &	Horizontal
P-1252A/B	Column Extract Pump	211-1210	2	Centrifugal	21	30	1.5	316 SS	Seal-less FV	150 &	Horizontal
P-1262A/B	Refinery Wash Column	211-1210	2	Centrifugal	153	127	10.0	316 SS	Seal-less FV	150 &	Horizontal
P-1331	Discharge Pump	211-1310	1	Centrifugal	500	51	10.0	316 SS	Seal-less FV	150 &	Horizontal
P-1351	Spent Solvent Hold Vessel Discharge Pump	211-1310	1	Centrifugal	20	123	5.0	316 SS	Seal-less FV	150 &	Horizontal
P-1361	Spent Gas Oil Hold Vessel Discharge Pump	211-1310	1	Centrifugal	25	105	3.0	316 SS	Seal-less FV	150 &	Horizontal
P-1422A/B	Solvent Purification	211-1410	2	Centrifugal	226	128	15.0	316 SS	Seal-less FV	150 &	Horizontal
P-1452A/B	Column Bottoms Pump	211-1410	2	Centrifugal	900	162	60.0	316 SS	Seal-less FV	150 &	Horizontal
P-1462A/B	Solvent Recovery	211-1410	2	Centrifugal	57	98	5.0	316 SS	Seal-less FV	150 &	Horizontal
P-1512A/B	Column Reflux Pump	211-1510	2	Centrifugal	440	59	15.0	316 SS	Seal-less FV	150 &	Horizontal
P-1522A/B	Solvent Recovery	211-1510	2	Centrifugal	15	61	2.0	316 SS	Seal-less FV	150 &	Horizontal
P-1552A/B	Hydrocarbon Recovery	211-1510	2	Centrifugal	127	122	10.0	7 CS 7	Double Mechanical FV	150 &	Horizontal
P-1562A/B	Hydrocarbon Recovery	211-1510	2	Centrifugal	49	136	5.0	304 SS	Seal-less FV	150 &	Horizontal
P-1712A/B	Wastewater Pump	211-1110	2	Centrifugal	15	106	5.0	Alloy 20	Seal-less FV	150 &	Horizontal
P-1722	Solvent Hold Tank Discharge Pump	211-1720	1	Centrifugal	40	175	7.5	316 SS	Seal-less FV	150 &	Horizontal
P-1760	Process Area Sump Pump	NA	1	Centrifugal	250	100	16.0	C8	Single Mechanical	100	Horizontal
P-1761	Peroxide Storage Area Sump Pump	NA	1	Air Discharge	25	30	NA	C8	Seal-less	100	NA
P-1762	Hold Tank Area Sump Pump	NA	1	Air Discharge	25	30	NA	C8	Seal-less	100	NA
P-1763	ERS Area Sump Pump	NA	1	Air Discharge	25	30	NA	C8	Seal-less	100	NA

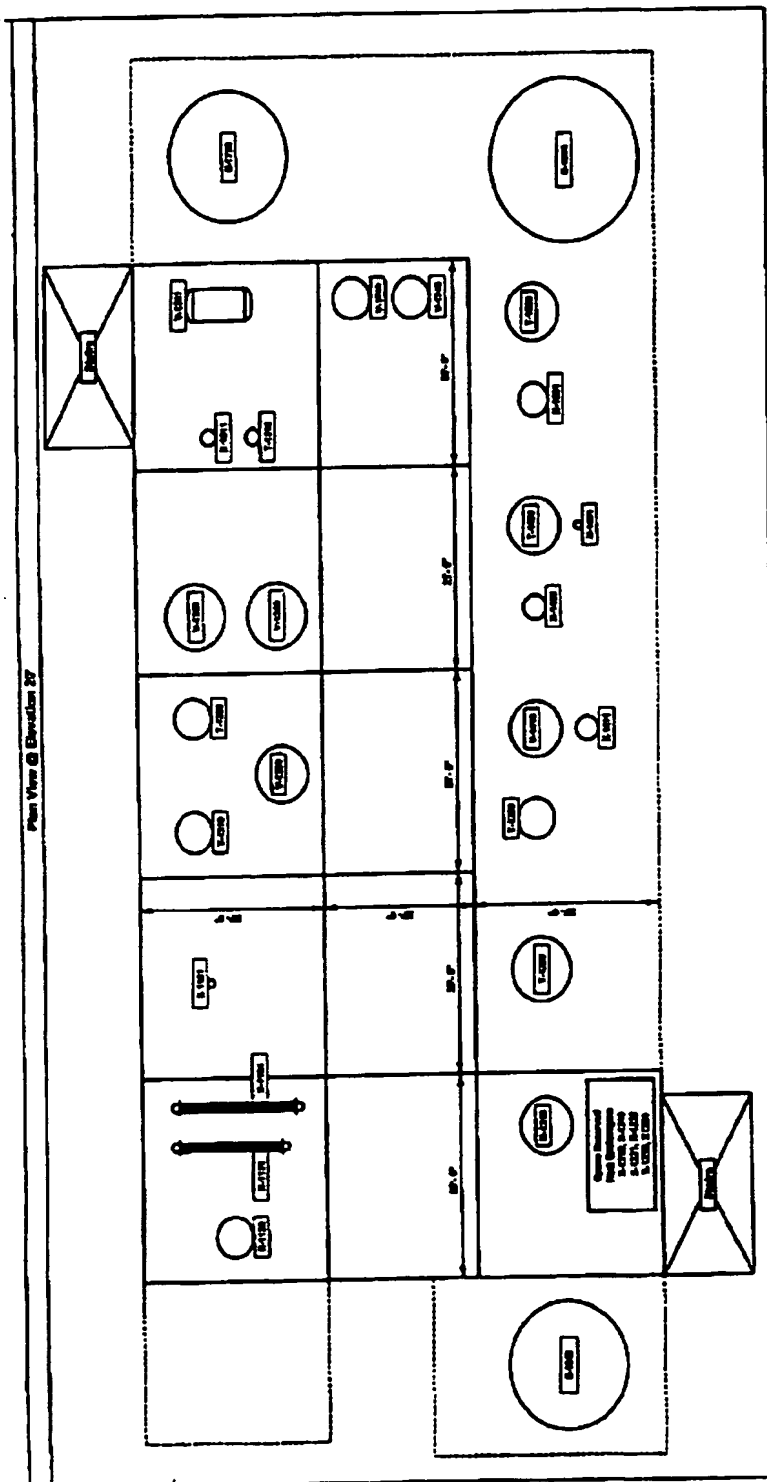
Pumps to the Wastewater Treatment with operator
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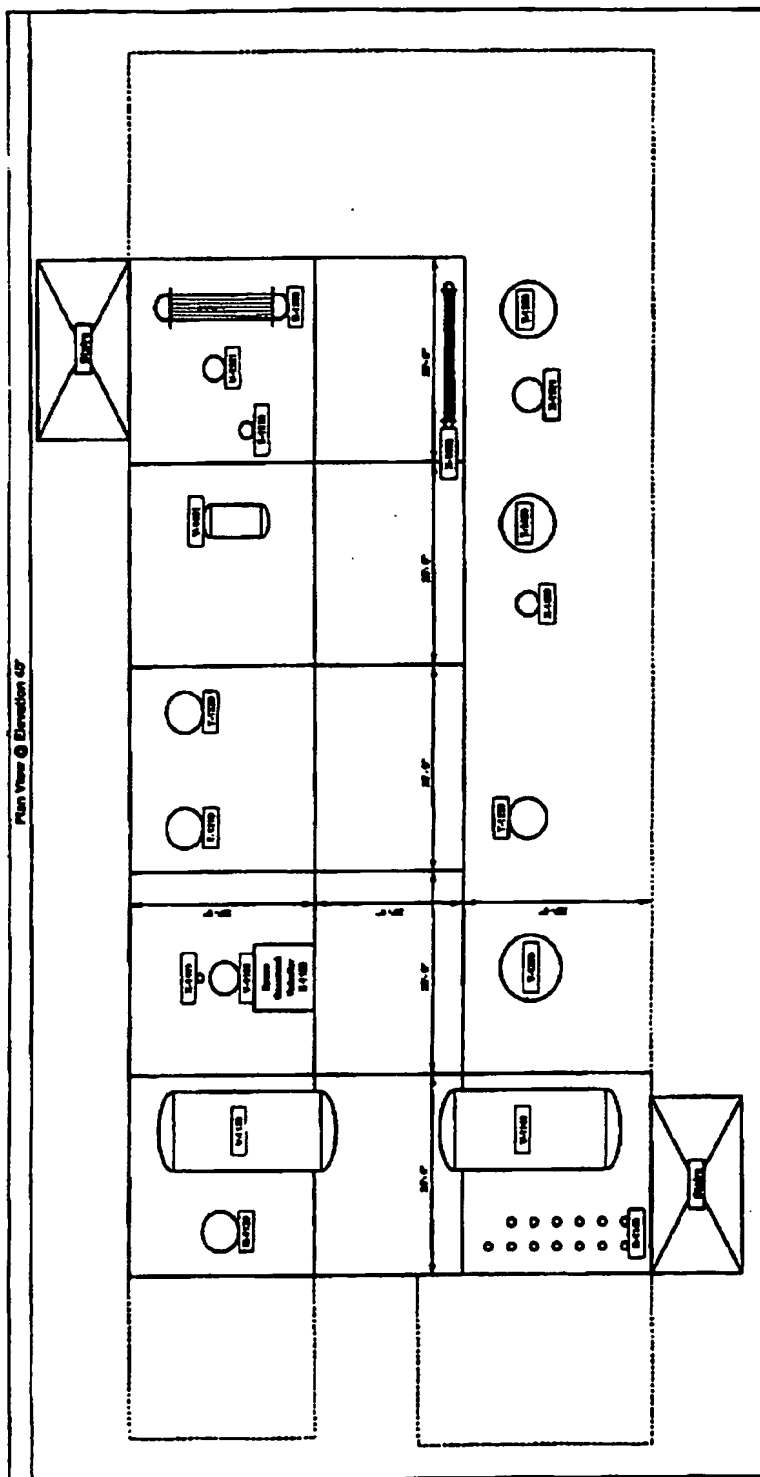
Other Equipment												
Item Number	Description	PER	Q	Type	D	L	Motor	MOC	Internal	DP	DT	Consumption
					Ind	Ind	hp			psig	F	lb/hr
A-1211	Deethyl Reactor Agitator	211-1210	1	Turbine	NA	NA	8.0	316 SS	NA	NA	682	27
R-1140	2nd Stage Oxidizer	211-1110	1	Pug Flow Reactor Mixer	10" Sch 20 Pipe	461	NA	Alloy 20	Alloy 20	50 & FV	682	NA
Packaging Systems												
Item Number	Description	PER	Q	Type	Capacity	Motor	MOC			DP	DT	Consumption
						hp				psig	F	lb/hr
Z-1590	Oxidizer System	NA	1	Mechanical Compressor	4 tons	7.5	CS					5.6
Z-1070	Hydrocarbon Recovery Column Vacuum System	211-1510	1	3 Stage Steam Jet System			316 SS			See Individual Components		
Item Number	Description	PER	Q	Type	Duty	Area	Size	MOC		DP	DT	Consumption
					min/hr	sq ft	inches	Shell	Tubes	psig	F	lb/hr
X-1071	1st Stage Vacuum Jet Condenser	211-1510	1	Tube BEM Shell & Tube	0.100	63.8	9" x 10"	316 SS	316 SS	50 & FV	682	120 & FV
X-1074	2nd Stage Vacuum Jet Condenser	211-1510	1	Tube BEM Shell & Tube	0.135	18.0	6" x 6" x 7'	316 SS	316 SS	50 & FV	682	120 & FV
X-1077	3rd Stage Vacuum Jet Condenser	211-1510	1	Tube BEM Shell & Tube	0.075	9.4	6" x 6" x 7'	316 SS	316 SS	50 & FV	682	120 & FV
Item Number	Description	PER	Q	Type		Overall Length	inches	MOC		DP	DT	Consumption
										psig	F	lb/hr
Y-1570	1st Stage Vacuum Jet	211-1510	1	Ejector		40		316 SS	NA	200 & FV	682	
Y-1573	2nd Stage Vacuum Jet	211-1510	1	Ejector		20		316 SS	NA	200 & FV	682	
Y-1576	3rd Stage Vacuum Jet	211-1510	1	Ejector		13		316 SS	NA	200 & FV	682	
Remarks												
One 5' Wide x 42" Diameter 2nd Stage Packed Turbine Operating at 75 RPM (12 Sample Run Sections @ 30' each, 13 - 480 degree Long Radius Bore with R ₁ = 1.5												
Services X-1553 with 25 wt % Ethylene Glycol at 10 P												
Suction Pressure = 5 mmHg; Air Leakage = 13 lb/hr												
Part of Vacuum System (Z-1070)												
Part of Vacuum System (Z-1070)												
Part of Vacuum System (Z-1070)												
Part of Vacuum System (Z-1070)												
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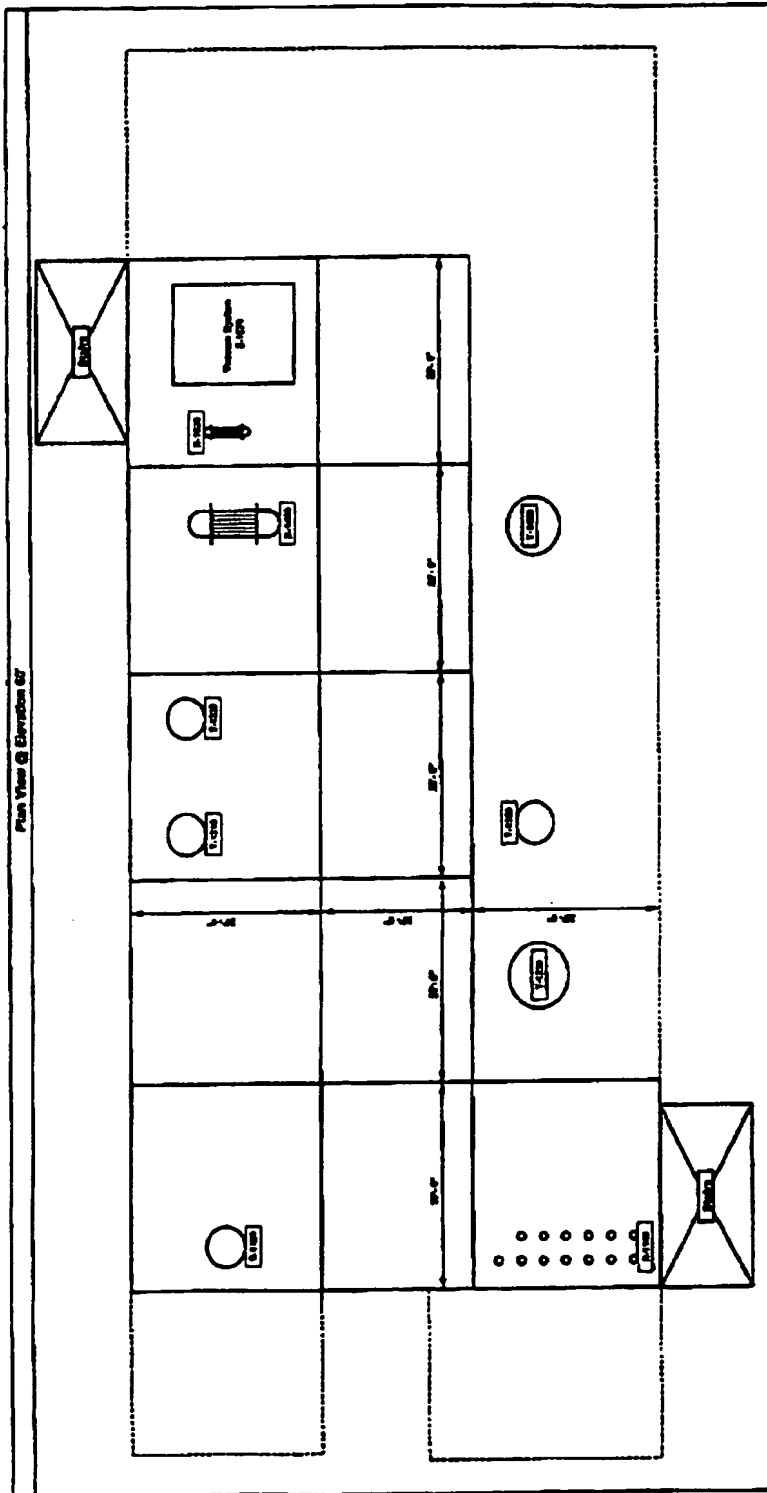












APPENDIX F - EQUIPMENT

Item Number	Description
A-1211	Destruct Reactor Agitator
P-1041	Peroxide Unloading Pump
P-1042A/B	Peroxide Feed Pump
P-1123A/B	1st Stage Oxidizer Oil Pump
P-1142A/B	Oxidant Recycle Pump
P-1182A/B	Water Flash Vessel Bottom Pump
P-1214A/B	Destruct Reactor Discharge Pump
P-1233A/B	Sulfur Extraction Column Extract Pump
P-1252A/B	Raffinate Wash Column Extract Pump
P-1282A/B	Raffinate Hold Vessel Discharge Pump
P-1331	Product Hold Tank Discharge Pump
P-1351	Spent Acetic Acid Hold Vessel Discharge Pump
P-1361	Spent Gas Oil Hold Vessel Discharge Pump
P-1422A/B	Solvent Flash Vessel Distillate Pump
P-1452A/B	Solvent Purification Column Bottoms Pump
P-1462A/B	Solvent Purification Column Reflux Pump
P-1512A/B	Solvent Recovery Column Bottoms Pump
P-1522A/B	Solvent Recovery Column Reflux Pump
P-1552A/B	Hydrocarbon Recovery Column Bottoms Pump
P-1562A/B	Hydrocarbon Recovery Column Reflux Pump
P-1712A/B	Wastewater Purge Pump
P-1722	Solvent Hold Tank Discharge Pump
P-1790	Process Area Sump Pump
P-1791	Peroxide Storage Area Sump Pump
P-1792	Hold Tank Area Sump Pump
P-1793	ERS Area Sump Pump
R-1120	1st Stage Oxidizer
R-1140	2nd Stage Oxidizer
R-1210	Destruct Reactor
S-1040	Hydrogen Peroxide Storage Tank

[illegible]

APPENDIX F – EQUIPMENT

Item Number	Description
S-1330	Product Hold Tank
S-1720	Solvent Hold Tank
T-1230	Sulfur Extraction Column
T-1250	Raffinate Wash Column
T-1310	Raffinate Polishing Column
T-1320	Raffinate Polishing Column
T-1450	Solvent Purification Column
T-1510	Solvent Recovery Column
T-1550	Hydrocarbon Recovery Column
V-1122	1st Stage Oxidizer Oil Decanter
V-1141	2nd Stage Oxidizer Oil Decanter
V-1160	Water Flash Vessel
V-1280	Raffinate Hold Vessel
V-1350	Spent Acetic Acid Hold Vessel
V-1360	Spent Gas Oil Hold Vessel
V-1410	Solvent Flash Vessel
V-1421	Solvent Flash Vessel Distillate Receiver
V-1461	Solvent Purification Column Reflux Decanter
V-1521	Solvent Recovery Column Reflux Drum
V-1561	Hydrocarbon Recovery Column Reflux Drum
V-1710	Wastewater Neutralization Vessel
V-1740	Non-Oxygen Containing Offgas Knockout Vessel
V-1745	Oxygen Containing Offgas Knockout Vessel
V-1780	Emergency Relief System Knockout Vessel
X-1121	Gas Oil Feed Heater
X-1124	1st Stage Oxidizer Discharge Interchanger
X-1161	Water Flash Vessel Reboiler
X-1212	Destruct Reactor Feed / Effluent Interchanger
X-1213	Destruct Reactor Feed Interchanger
X-1231	Sulfur Extraction Column Solvent Interchanger

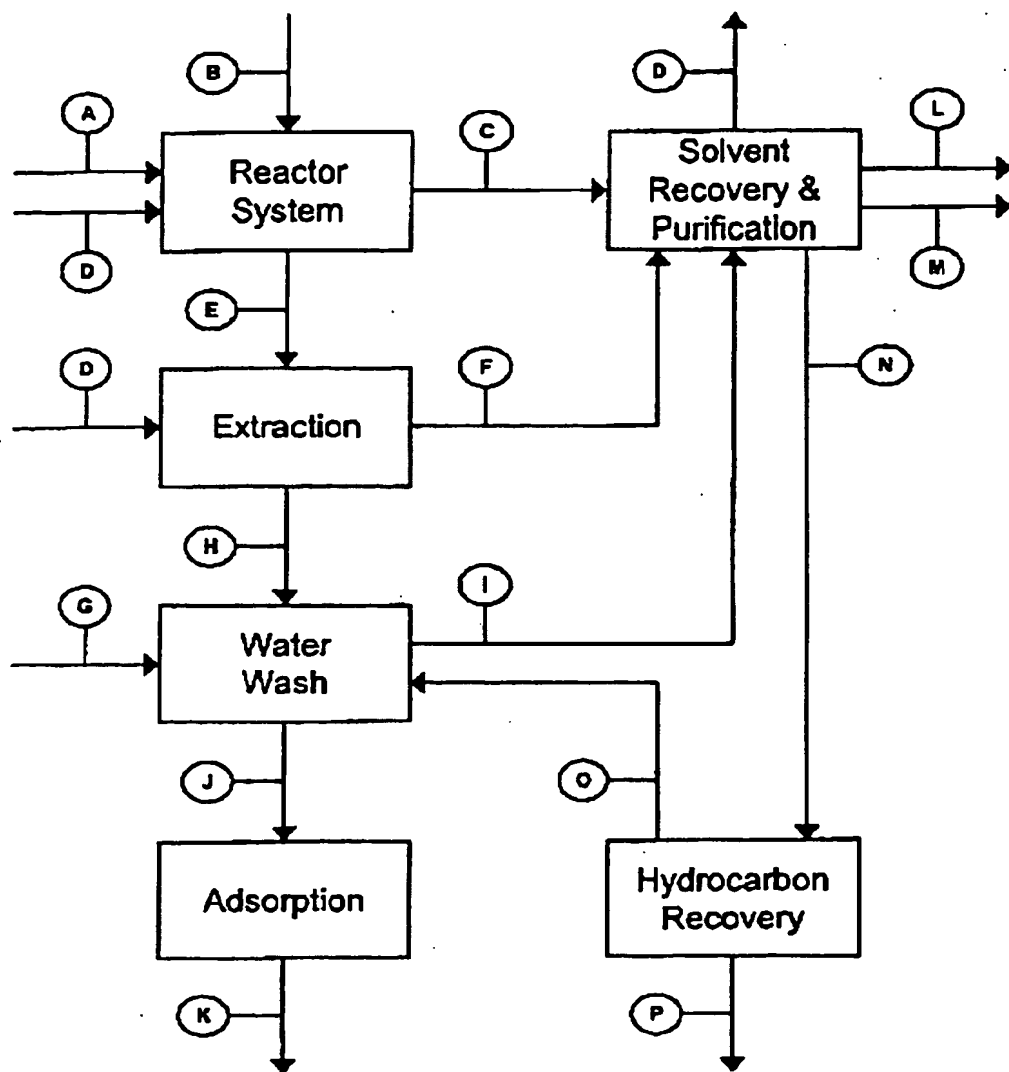
[illegible]

APPENDIX F – EQUIPMENT

Item Number	Description
X-1232	Sulfur Extraction Column Solvent Cooler
X-1233	Sulfur Extraction Column Feed / Effluent Interchanger
X-1234	Sulfur Extraction Column Feed Cooler
X-1411	Solvent Flash Vessel Reboiler
X-1420	Solvent Flash Vessel Overhead Condenser
X-1451	Solvent Purification Column Trim Reboiler
X-1460	Solvent Purification Column Overhead Condenser
X-1463	Solvent Purification Column Water Distillate Cooler
X-1511	Solvent Recovery Column Reboiler
X-1520	Solvent Recovery Column Overhead Condenser
X-1551	Hydrocarbon Recovery Column Reboiler
X-1553	Hydrocarbon Recovery Column Bottoms Cooler
X-1560	Hydrocarbon Recovery Column Overhead
X-1563	Hydrocarbon Recovery Column Vent Condenser
X-1711	Wastewater Neutralization Vessel Cooler
X-1721	Solvent Hold Tank Cooler
Z-1570	Hydrocarbon Recovery Column Vacuum System
Z-1580	Chiller System

[illegible]

Figure 1 - Block Flow Diagram



APPLICATION DATA SHEET

APPLICATION INFORMATION

Application Type::	PROVISIONAL
Subject Matter::	UTILITY
CD-ROM or CD-R?::	NONE
Title::	METHOD AND APPARATUS FOR CONVERTING SULFUR-CONTAINING DISTILLATES, AND COMPOSITIONS OBTAINED THEREBY
Attorney Docket Number::	244547US0PROV
Total Drawing Sheets::	1

INVENTOR INFORMATION

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CORRESPONDENCE INFORMATION

Correspondence Customer Number::	22850
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REPRESENTATIVE INFORMATION

Representative Customer Number:: 22850

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 37 CFR 1.53(c).

Docket Number 244547US0PROV

INVENTOR(s)/APPLICANT(s)

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TARABOCCHIA	John		
JONES	Jerald	A.	
LEININGER	Stefan		

☒ Additional inventors are named on separately numbered sheets attached hereto.

TITLE OF THE INVENTION (280 CHARACTERS MAX)

METHOD AND APPARATUS FOR CONVERTING SULFUR-CONTAINING DISTILLATES, AND COMPOSITIONS OBTAINED THEREBY

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ENCLOSED APPLICATION PARTS

☒ Specification Number of Pages: 65

☐ CD(s), Number

☒ Drawing(s) Number of Sheets: 1

☒ Other (specify):

White Advance Serial Card
Application Data Sheet

METHOD OF PAYMENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☒ A check or money order is enclosed to cover the Provisional Filing Fees

☐ Credit card payment form is attached to cover the Provisional Filing Fees in the amount of _____

☒ The Director is hereby authorized to charge filing fees and credit any overpayment to Deposit Account Number 15-0030

PROVISIONAL \$160.00
FILING FEE
AMOUNT

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☐ No.

☒ Yes, the name of the U.S. Government agency and the Government contract number are:

DE-FC26-01BC15281; W(A)-02-003, CH-1087

Respectfully Submitted,

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PROVISIONAL APPLICATION FILING ONLY

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/US04/034496

International filing date: 20 October 2004 (20.10.2004)

Document type: Certified copy of priority document

Document details: Country/Office: US
Number: 60/513,210
Filing date: 23 October 2003 (23.10.2003)

Date of receipt at the International Bureau: 10 January 2005 (10.01.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse